STUDIES ON SOME NEW TRANSITION METAL COMPLEXES OF THE SCHIFF BASES DERIVED FROM QUINOXALINE - 2 - CARBOXALDEHYDE

Thesis submitted to the
Cochin University of Science and Technology
in partial fulfilment of the requirements
for the degree of
Doctor of Philosophy

S. MAYADEVI

DEPARTMENT OF APPLIED CHEMISTRY
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
KOCHI - 682 022

AUGUST 1997

DECLARATION

I hereby declare that the work presented in this thesis is based on the original work done by me under the guidance of Dr. K. K. Mohammed Yusuff, Professor, Department of Applied Chemistry, Cochin University of Science and Technology, Kochi-682 022, and further that no part of this thesis has been included in any other thesis submitted previously for the award of any degree.

S. Mayadevi

Kochi-22

06-08-1997

CERTIFICATE

This is to certify that the thesis bound herewith is an authentic record of research work carried out by the author under my supervision in partial fulfilment of the requirements for the degree of Doctor of Philosophy of Cochin University of Science and Technology.

Kochi -22
06-08-1997

Dr. K. K. Mohammed Yusuff
(Supervising Teacher)

ACKNOWLEDGMENT

This is a statement of gratitude for a number of wonderful persons who had bestowed selfless help and consideration upon me, during my period of research.

The work presented here owes its existence first and foremost to my respected supervising guide Dr. K. K. Mohammed Yusuff, Professor, Dept. of Applied Chemistry, Cochin University of Science and Technology. He led me through the complications of the subject as a true guide. Without him this work would not have been materialised. I wish to express my deep gratitude to Prof. P. Madhavan Pillai, Head of the department, for his constant encouragement during the course of this study.

I would like to place on record my heartfelt thanks to Prof. K. L. Sebastian, IISc Bangalore for the kind and valuable help he rendered.

My sincere thanks are due to Prof. S. Sugunan, Prof. V. N. Sivasankara Pillai (School of environmental studies), Dr. Prathapachandra Kurup, Dr. S. Prathapan and Dr. P. A. Unnikrishanan for their cooperation.

I stand in debt to my beloved colleagues, Dr. N. Sridevi, Dr.R. Sreekala, Dr.C. Krishnakumar, Dr.Jose Mathew, Dr.Sudha George Valavi, Dr. N. Saravanan, Ms.Preetha G. Prasad and Ms. Rani Abraham for their timely help at all stages of this work. Words cannot be strong enough to express my gratitude for them.

My thanks are also due to Mr. K. Anas and Mr. Binoy Jose for help they had done during the thesis work.

I am thankful to all research scholars, students and non-teaching staff of the Department of Applied Chemistry for their cooperation.

I thank RSIC Madras, and CSMCRI Bhavanagar for providing me the necessary spectral facilities. I am grateful to UGC, New Delhi for the award of a research fellowship.

S.MAYADEVI

PREFACE

This thesis deals with the synthesis, characterisation and catalytic activity studies of some new transition metal complexes of the Schiff bases, derived from quinoxaline-2-carboxaldehyde. The model complexes derived from specially designed and synthesised Schiff bases help us to understand the chemistry of biological systems. Schiff bases derived from heterocyclic aldehydes like quinoxaline-2-carboxaldehyde provide great structural diversity during complexation. The Schiff bases synthesised in the present study are quinoxaline-2-carboxalidene-2-aminophenol (QAP), quinoxaline-2-carboxaldehyde semicarbazone (QSC), quinoxaline-2-carboxalidene-o-phenylenediamine (QOD) and quinoxaline-2-carboxalidene-2-furfurylamine (QFA). The elucidation of the structure of these complexes is done using conductance, magnetic susceptibility measurements, infrared, UV-Vis and EPR spectral studies.

The thesis comprises of eight chapters. Chapter I of the thesis presents an introduction of the metal complexes of Schiff bases derived from various aromatic aldehydes. Chapter II gives details of the preparation and purification of the ligands. Various techniques employed to characterise the metal complexes are also given in this chapter.

Chapter III, IV and V of the thesis deal with the synthesis and characterisation of the metal complexes of the ligands, QAP, QSC, QOD and QFA.

The complexes were screened for their catalytic activity in the well-known reaction of oxidation of ascorbic acid to dehydroascorbic acid. The results of these studies are presented in Chapter VII. In continuation of this work, a detailed kinetic study was made on the catalytic oxidation of ascorbic acid by the copper complex of the ligand QAP, in order to understand the mechanism of catalysis by the copper complexes. The results thus obtained were presented in Chapter VIII.

CONTENTS

Chapter IV QUNOXALINE-2-CARBOXALDEHYDE SEMICARBAZONE COMPLEXES OF Mn(II), Fe(III), Co(II), Ni(II) AND Cu(II)

Chapter V QUINOXALINE-2-CARBOXALIDENE-*O*-PHENYLENEDIAMINE COMPLEXES OF Mn(II), Fe(III), Co(II), Ni(II) AND Cu(II)

Chapter VI QUNIXALINE-2-CARBOXALIDENEFURFURYLAMINE COMPLEXES OF Mn(II), Fe(III), Co(II), Ni(II) AND Cu(II)

Chapter VII CATAYLITIC ACTIVITY STUDIES OF THE COMPLEXES IN THE OXIDATION OF ASCORBIC ACID TO DEHYDROASCORBIC ACID

Chapter VIII KINETIC STUDY OF THE OXIDATION OF ASCORBIC ACID USING [Cu(QAP)$_2$] AS CATALYST

CHAPTER I

INTRODUCTION

Schiff bases are those compounds containing the azomethine group (-RC = N-) and are usually formed by the condensation of a primary amine with an active carbonyl compound. Bases which are effective as coordinating ligands bear a functional group, usually -OH, sufficiently near the site of condensation that a five or six membered chelate ring can be formed upon reaction with a metal ion[1].

Metal complexes of Schiff bases represent an important and interesting class of coordination compounds[2-8]. The ability of metal centres to display different coordination numbers as well as a variety of coordination modes makes it difficult to establish the corresponding stereochemical peculiarities of Schiff base complexes and therefore synthesis and characterisation of such complexes have always been a challenge to coordination chemists. Since the seminal works by Ettling et al.[9], metal-chelate Schiff base complexes have continued to play the role of one of the most important stereochemical models in main group and transition metal coordination chemistry due to their preparative accessibility, diversity and structural variability. Apart from this, aspects of the topic are of relevance to those whose interest include organic synthesis in the presence of metal ions, areas of metal ion catalysis, and biochemical reactions involving Schiff bases. Two excellent reviews of Schiff base complexes appeared in 1960[1] and 1966[9]. The first of these, which was written by B. O. West, stressed the chemistry of inner complexes, whereas the latter dealt in detail with the chemistry of salicylaldimines, β-ketoamines and closely related ligands. A monograph dealing with the stereochemistry of Schiff base complexes as well as the aspects of behaviour of such complexes in solution, has also been published[10].

During the last few years a significant amount of information related to the synthesis and characterisation of Schiff bases and their complexes with several metal ions has appeared in the literature[11-15].

Synthetic Methods of Schiff Base Complexes

a. Direct ligand synthesis followed by complexation:

The preparation and isolation of the free Schiff base ligand followed by complexation with a metal ion has traditionally been the usual method for the preparation of metal ion complexes. The isolation of the free Schiff base before reaction with a metal ion has certain advantages compared to the *in situ* preparations. The reactants used to prepare Schiff bases are often good coordinating ligands. Therefore a small excess of one of the reactants will lead to the contamination of the product, if not removed before the Schiff base is complexed with a metal ion. In the direct type of ligand synthesis, the removal of impurities can be achieved by normal purification techniques. Furthermore, characterisation of the free ligand enables a comparative study to be made of its physico-chemical properties with those of the corresponding metal complexes. In this manner the elucidation of the structure of the complexes may be facilitated.

b. Synthesis in situ:

In this class of synthesis the formation of the Schiff base occurs in the presence of the metal ion to give the corresponding metal chelate directly. Metal ions assist the formation of Schiff bases by creating stable complexes, thus producing a favourable overall free energy of reaction[16]. Furthermore, the metals were found to catalyse these reactions by serving as a reaction template. Two types of template effects have been recognised[17] in the formation *in situ*, of Schiff base complexes, When the role of the metal ion is to organise or orient the reacting species such that the required product forms in higher yield then this amounts to a sterically directed kinetic mechanism and has been named the kinetic template effect. If however the metal ion removes the Schiff base from an equilibrium by complexation, then a thermodynamic template effect is operating. An interesting Schiff base complex of copper was prepared by the reaction of salicylaldehyde with glycine in the presence of copper(II) ion[18].

c. Metal ion induced rearrangements:

Many 2-hydroxy or 2-thiol amines react with aldehydes to give certain heterocyclic compounds other than Schiff bases[19]. Nevertheless, in solution, it has been shown that both products exist in equilibrium with their respective tautomeric Schiff bases. Addition of metal ions results in the isolation of high yields of the Schiff base complexes[20]. It has been postulated that the metal ion sequesters the Schiff base form from the equilibrium and hence thermodynamic template effects appear to operate in these reactions. We can expect a high yield of the complex if the metal complex produced is only slightly dissociated in solution or if it gets precipitated from the solution. In certain cases competing equilibria are involved and the isolation of the required complex depends on a number of factors, including the pH of the solution, the nature of the solvent, and the relative solubilities of the species present. Generally Schiff base formation is found to be favoured in basic media.

d. Oxidation of Coordinated Secondary Amines:

Another route that is sometimes used to prepare Schiff bases, is the oxidative dehydrogenation of the corresponding secondary amines. This may be effected in the presence of suitable metal ions such that a Schiff base compound is obtained readily. The use of redox reactions to generate imine linkages *in situ* provides a reaction type of great versatility since a wide range of chemical oxidising agents are available whose mode of action depends upon the reaction conditions as well as on the particular metal ion present. Electrochemical oxidations can also be used. By the choise of suitable conditions, selective reactions can sometimes be used to produce a series of closely related complexes which differ only in their degree of unsaturation. Reported cases indicate that the metal ion can influence the rate of formation of the complexes as well as the structure of the redox product[21].

e. Amine Exchange Reaction:

New Schiff base complexes can be synthesised by carrying out amine exchange reactions on existing Schiff base complexes[22-26]. These reactions can be compared to the well known transamination reactions of biological systems. The reactions may proceed by an initial attack of the exchanging amine on the electron-deficient carbon of the polarised imine linkage, and it appears that these reactions are equilibrium controlled. An excess quantity of exchanging amine is usually used in these cases. Product yield depends on the basicity of the exchanging amine. A high yield of product can be obtained when the reacting amine is significantly more basic than the displaced amine.

f. Metal Ion Exchange Reactions:

Schiff base complexes containing a labile metal ion can be used for metal exchange reactions[27-29]. Chiefly complexes of salicylaldimines or β-ketoimines have been employed for the synthesis of such complexes[28,29]. An advantage of metal exchange as a synthetic method is that often side reactions can be minimized by adopting this procedure.

To understand the chemistry of formation of Schiff bases and their metal complexes, it is always wiser to choose the systems derived from salicylaldehyde as the prototype because these compounds as a class have been the subject of thorough investigation. Metal complexes of salicylaldimines are obtained by direct reaction of Schiff base and metal ions, template reaction or by reaction of amines with bis or tris salicylaldehyde metal complexes. The condensation of amines with coordinated aldehydes or ketones was first employed by Schiff[30] to prepare bis(salicylaldimino)copper complexes. Polarisation of the carbonyl group on coordination to a positive metal ion will result in the carbonyl carbon becoming more susceptible to nucleophilic attack by the lone pair of the amine. However a carbonyl oxygen is usully a very poor donor towards most metal ions and thus in solution, it is readily displaced from the coordination sphere by solvent molecules. But the carbonyl group can be made to remain coordinated in solution,and thus Schiff base condensation can be facilitated, if the carbonyl containing moiety contains another donor atom which enables the formation of a strong chelate ring. Many such reactions involving coordinated salicylaldehyde have been reported[9].

The Schiff bases derived from salicylaldehyde are among the most thoroughly studied ligand systems. The particular advantage of such ligand systems is the flexibility of the synthetic procedure which has allowed the preparation of a wide variety of complexes. In this way it has been possible to effect certain stereochemical and electronic changes more or less systematically in a graded series of complexes by structural variations of the ligand. It is this feature of salicylaldimine complexes which is principally responsible for their current significance.

Salicylaldimines frequently show enol-imine tautomerism in solution. Some structural features were observed in the case of substituted Schiff bases; for example, the influence of halogen substitution on the electronic distribution of salicylaldimine ligands has been evaluated through a detailed analysis of vibrational bands[31].

Complexes formed by salicylaldimines are of three main structural types as shown in Fig.1.

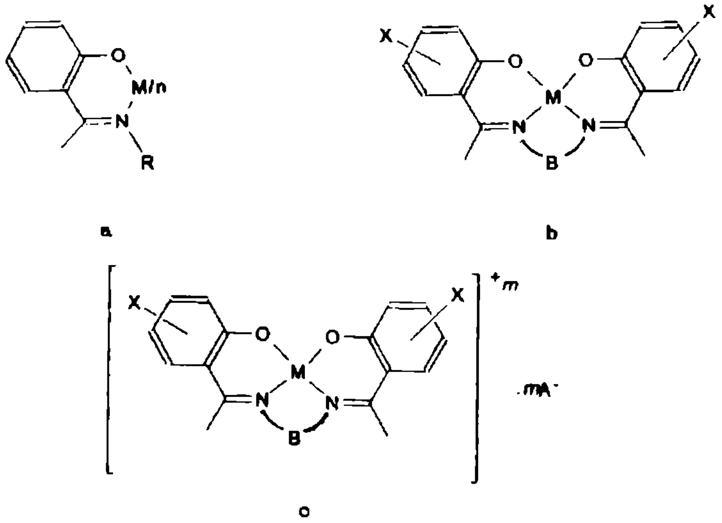


Fig. 1.1
R, X and B are substituents on nitrogen, ring and bridging group respectively.

Condensation with primary amines (aryl or alkyl) usually results in the formation of Schiff bases of type a (Fig. 1.a) which can form bidentate complexes. In these complexes stability of the planar form of the complex is dependent on the steric requirements of the substituent R which, if sufficiently demanding, may force a nonplanar configuration in those cases. Condensation of salicylaldehyde with diamines gives compounds with structure shown in figure 1.b. They generally act as quadridentate ligands. The third type of Schiff base formed by salicylaldehyde are given in figure 1.c. Such complexes usually contain M = Ni(II), Cu(II), VO and UO_2, and L = O. They are much less thoroughly studied.

In quadridentate ligands it is seen from the X-ray data that N_2O_2 unit is planar. The metal atom lies above the N_2O_2 plane. From magnetic and structural data, it is clear that there is considerable internuclear interaction in these type of complexes at least in the solid state[32-35]. In these complexes the four donor atoms are almost always coplanar with small deviations towards a tetrahedral geometry. The iron complexes show the most significant deviations from planarity when compared with those of cobalt and copper.

Only a modest number of complexes containing manganese and iron in their bi or trivalent state have been reported. Manganese(II) complexes of salicylaldimines are found to be high spin, although in some reported cases the moments are lower than the spin only value[36,37]. The lower moments observed for some of the complexes may be due to the partial oxidation of manganese(II) to manganese(III) or due to the spin exchange in the solid phase.

Ferrous and ferric ions form salicylaldimine complexes of all the three structural types. Most of these complexes are high spin. Fe(III) ion also forms dimeric complexes in which case the magnetic moment is considerably reduced from the spin only value due to anti ferromagnetic interaction.

There is a lot of information in the literature relating to nickel(II) complexes with bidentate Schiff bases[38–42]. The incorporation of α-branched substituents and particularly the t-butyl group results in the destabilization of the planar configuration. In the case of copper(II) complexes such an incorporation would lead, to a gradual distortion of a planar structure towards a tetrahedral one. Whereas in the case of the nickel(II) complexes, these changes result in the shift of the planar $\rightleftharpoons$ tetrahedral equilibrium to the right in solution and thus tetrahedral structure in solid state will be stabilised. The cobalt(II) ion is more inclined to form tetrahedral configuration.

Chelate complexes of salicylaldimine with a structure incorporating five and six membered metallocyclic moieties with the same metal centre were prepared from Schiff bases of salicylaldehyde and o-aminophenol. Umbrella conformation occurs in dimeric pentacoordinated complexes containing solvent molecules or other ligands in the axial sites. Cobalt(II) complexes of the Schiff base derived from salicylaldehyde and *o*-phenylenediamine crystallise as planar and umbrella conformational isomers within the same unit cell[43].

Salicylaldehyde semicarbazones, a potentially tridentate ligand, is found to act as a bidentate monoanion because of the non-participation of the carbonyl oxygen[44] of the semicarbazone moiety. This seems to be a typical ligation behaviour of aryl derivatives of semicarbazones and has been termed the flip-tail bidenticity.

The effect of substitution by nitro groups in nickel(II) complexes with Schiff bases derived from salicylaldehydes, α-hydroxy naphthaldehydes and aniline has been the subject of many reports[39,40,45]. These compounds showed intramolecular hydrogen bonds and tautomeric equilibria in some cases[41]. The electronic effects due to the presence of nitro groups on salicylaldimines were not similar to those observed for α-hydroxy naphthaldimines[46]. Electronic spectroscopy results indicated that in these cases, the nickel(II) complexes change their structures on going from solution to solid phase, the changes depending on the donor character and polarity of the solvent. Holm et al and others reported, several years ago, the temperature dependent probable association or conformational equilibrium in solution between planar and tetrahedral species for Ni(II) complex of N-alkyl-salicylaldimines[46-51].

No substantial solvent effects were found in the electronic spectra of nickel(II) tetradentate Schiff bases; while noticeable changes are obtained in the case of copper(II) analogues[52]. These facts can be explained in terms of the molecular orbitals involved in the electronic transition[53]. In addition, the stereochemistry of these complexes exhibited marked differences depending on the substituent in the bases or on the length of the methylene chain[54-57].

In addition to these complexes salicylaldimines are also reported to form linear or bifurcated sexadentate Schiff bases[58,59].

Schiff bases and their complexes derived from heterocyclic aldehydes and amines are rather rare. Most of the informations now available are about those moieties which include one or more pyridine rings. Metal complexes of the Schiff bases derived from Pyridine-2-caboxaldehyde are reported to be synthesised by direct reaction of Schiff bases and metal ions[60], template reaction or by the reaction of the aldehyde with preformed metal complexes formed by the interaction of the corresponding amines with metal salts. Generally it is not desirable to use a coordinated amine for such a reaction, since coordination severely impaires the nucleophilic character of the nitrogen. It has been suggested that the heteroatom of the pyridine-2-carboxaldehyde ring may first effect amine displacement prior to Schiff base condensation[61,62].

Schiff bases with an electron withdrawing heterocyclic ring system exhibit many interesting structural features as the ligand field of such ligands are expected to be weaker than the corresponding one with aromatic systems. Such multidentate Schiff bases can be obtained from the interaction of pyridine-2-carboxaldehyde with diamines[63] and triamines[64] and other aminocompounds[65]. The condensate of pyridine-2-carboxaldehyde and 1, 8-diamino-3, 6-dithiaoctane has been shown to form linear sexadentate complexes having the same structure as that of the complex formed by salicylaldimine with the same amine[66]. Certain bifurcated sexadentate complexes of Schiff bases derived from pyridine-2-carboxaldehyde have also been reported[67]. The structures of these types of complexes are such that they offer a plausible racemization mechanism.

The pyridine-2-carboxaldehyde thiosemicarbazones are among the most studied thiosemicarbazone from the chemical and structural point of view as well as from the biological point of view[68-74]. Thiosemicarbazones of pyridine-2-carboxaldehyde has marked antitumour activity[75]. This ligand has high affinity for copper(II) ion. The copper complex is found to be more potent[76], as determined by single-cell survival of Chinese hamster ovary cells. A possible mechanism of antitumour activity of the complex may be due to the reduction of Cu(II) to Cu(I) complex by thiols followed by release of the pyridine-2-carboxaldehyde thiosemicarbazone ligand and then the binding of this to inhibit ribonucleoside diphosphate reductase action.

The nature of binding of pyridine-2-carboxaldehyde thiosemicarbazones with Ehrlich ascites tumour cells has been described by Petering and coworkers[77]. The compound is found to inhibit cellular DNA formation at low concentrations, but the RNA formation is found to be less sensitive. The binding sites are indicated to be glutathione thiol groups, confirming the earlier observations of Bushnell and Tasang[78].

Though quinoxaline is known as an excellent bridging ligand among nitrogen heterocycles, reports of compexes derived from its derivatives are scanty. Iron(III), cobalt(II), and copper(II) complexes of the Schiff base derived from quinoxaline-2-carboxaldehyde and 2-aminocyclopent-1-ene-1-dithiocarboxylic acid (L) have been reported[79]. The complexes have the general formula [MLCl] for the cobalt(II), nickel(II) and copper(II) complexes. The iron(III) complex has the formula [FeLCl(OH)(H_2O)]. Octahedral and tetrahedral structures have been assigned for the iron(III) and cobalt(II) complexes respectively, while nickel(II) and copper(II) complexes have square planar geometry. The ligand acts as a tridentate ligand coordinating through one of the sulphur atoms, the azomethine nitrogen atom and also through nitrogen atom of the quinoxaline ring.

Iron(III), cobalt(II), nickel(II) and copper(II) complexes of another Schiff base ligand derived from quinoxaline-2-carboxaldehyde and amino group supported on cross linked polystyrene (L) have been reported[79]. The empirical formula for the iron(III) complex is

$[FeL(OAc)_3(H_2O)_2]$. For the cobalt(II), nickel(II) and copper(II) complexes it is $[ML(OAc)_2(H_2O)]$ where OAc represents an acetate group. Infrared spectra indicate that in all the complexes, bonding of Schiff base is through the azomethine nitrogen atom and not through the nitrogen atom of the quinoxaline ring. Based on the electronic spectra and magnetic behaviour, octahedral and tetrahedral structures have been assigned respectively for the iron(III) and cobalt(II) complexes and square planar structures for the nickel(II) and copper(II) complexes.

Spectral and thermal studies on new complexes of iron(III), cobalt(II), nickel(II) and copper(II) with a Schiff base derived from quinoxaline-2-carboxaldehyde and glycine have been reported. A dimeric octahedral structure involving Cl and OH bridges has been proposed for these complexes[80]. Synthesis, characterisation and cytotoxicity of new quinoxaline-2-carboxaldehyde thiosemicarbazone (QTSC) complexes of cobalt(III), nickel(II) and copper(II) have been studied[81]. The complexes have the empirical formulae, $[Co(QTSC)_2]X_2$, $[Ni(QTSC)_2(OAc)X]$ and $[Cu(QTSC)(OAc)(H_2O)]_2$ where X = Cl/Br and OAc = acetate group. The magnetic and spectral data suggest a distorted octahedral geometry for the complexes. The copper complex appears to be dimeric with bridging acetate groups. The ligand acts as a uninegative tridentate NNS donor in the cobalt and copper complexes, while it acts as a neutral bidentate NS donor in the nickel complexes. The cytotoxicity of the cobalt(III) complexes was determined *in vitro* as well as in tissue culture. The chloro complex was found to have greater cytotoxic activity than the bromo complex.

Manganese(II), iron(III), cobalt(II), nickel(II) and copper(II) complexes of the Schiff bases derived from 3-hydroxyquinoxaline-2-carboxaldehyde were prepared. These Schiff bases were prepared by the condensation of the aldehyde with ethylenediamine (QED), o-phenylenediamine (QPD), hydrazine (QHD) and diethylenetriamine (QDT)[82]. Due to the comparatively weaker ligand field, the d level splitting is lesser in the complexes synthesised from the above Schiff bases. The complexes, therefore, show interesting magnetic properties. Furthermore, the nature of the ligands impose a particular geometry on the complexes. The ligand QED is dibasic and tetradentate and is expected to give square planar complexes, but all the complexes of QED synthesised are dimeric in nature. This happens only because the flexible ligand permits some distortion from a strictly planar structure. In the dimer the metal atom may probably be out of the plane of the donor atoms. As QPD does not favour such a distortion, it yields only monomeric complexes. The stereochemistry of QHD is not suitable for the coordination of all the four donor atoms to a single metal ion. Hence the ligand is found to form dimeric complexes with interesting structures. The QDT forms dimeric complexes in the cases of manganese(II) and iron(III). Spin-crossover equilibria is observed in the iron complex of QDT. Anomalous magnetic behaviour is obtained in the case of nickel complexes.

Manganese(II), iron(III), cobalt(II), nickel(II) and copper(II) complexes of the Schiff bases derived by the condensation of

3-hydroxyquinoxaline-2-carboxaldehyde with o-aminophenol, semicarbazide hydrochloride, furfuryl amine and thiosemicarbazide were prepared and characterised[83] . These complexes were screened for their catalytic activity in the oxidation of 3,5-ditert-butylcatechol to the corresponding quinone and found that most of the complexes are catalytically active.

Catalysis by Schiff base complexes

Schiff base complexes catalyse reactions like hydrolysis, carboxylation, decarboxylation, elimination, aldol condensation and redox reactions[84-86]. They also exhibit antifungal and antibacterial action.

Cobalt(II) complexes of Schiff base ligands derived fromo-phenylenediamine have been prepared,and the catalytic activation of oxygen using these complexes has been investigated[87].

The metal ion catalysed disproportioation of H_2O_2 has received much attention, because of the catalytic action of a heme iron enzyme, i.e, catalase, which enhances the decomposition of hydrogen peroxide dramatically[1]. Activity of copper(II) complexes of (salicylidene) amino acid Schiff bases have been tested towards the decomposition of hydrogen peroxide[88]. Detailed kinetic investigations for the disproportionation of hydrogen peroxide catalysed by the complexes of the general formula, $Cu(sal:aa)H_2O].nH_2O$ (where sal:aa = salicylideneaminoacid Schiff base derived from the condensation of salicylaldehyde and glycine/L-valine/L-methionine; n = 0 or 2) have been reported are discussed. The decomposition of hydrogen peroxide catalysed by the above complexes conform to Michaelis-Menton type kinetics.

Development of an excellent metal-complex catalyst for an asymmetric epoxidation of unfuctionalised olefins has been of great concern. Optically active salen-manganese(III) complexes were recently found to be effective catalysts for the enantioselective epoxidation, using terminal oxidants such as iodosyl benzene[89] sodium hypochloride[90] and hydrogen peroxide[91,92]. (Chem. Let. (1994) 1259)

Oxidation of various olefins have been carried out using the Mn (III) complex of Schiff bases derived from the condensation of salicylaldehyde and its derivatives with diaminopropanol, and the binuclear Mn(II) and Fe(III) complexes of Schiff bases obtained by the condensation of pyridene aldehyde with m- and p- phenylenediamine[93].

Copper(II) schiff base complexes were found to act as catalysts for the oxidative coupling of phenols[94]. They also act as catalysts for the oxidation of phenols to quinones. These complexes usually form adducts with oxygen molecules. Information about many such complexes which can bound revesibly with dioxygen are available in the review by Basolo et al[95].

Cobalt(II) complexes of aromatic Schiff bases form oxygenated complexes at lower temparatures ($0^{o}C$) possibly because these Schiff bases can readily donate electron density to the metal ion. Cobalt(II) complexes with the Schiff base ligands such as Co(Salen) [where Salen = N, N'-bis(salicylaldehyde)ethylenediaminedianion] and its analogues have been the first and most extensively investigated as reversible oxygen carriers[96-98]. Much attention has been paid on the reaction mechanism and the molecular structure of the oxygenated complexes. The molecular structure of some of the 1:2 adducts of dioxygen with Co(Salen) was confirmed in solution by EPR studies and dioxygen absorption measurements. Four coordinated planar Co(II) Schiff base readily bind dioxygen in the presence of suitable monodentate Lewis bases such as amines and solvents which provide electron density at the metal centre and this causes additional stabilization of the cobalt(II)-O_2 bond. Yuriko et al[99] have studied the high dioxygen uptake by hetero-metal binuclear Co(II)-Fe(II) Schiff base complex systems in dimethylsulphoxide under nitrogen and air by spectrophotometry, cyclic voltammetry and dioxygen uptake measurements.

A large variety of polymer supported Schiff base complexes were synthesised and they are found to be very good oxygen carriers. The cobalt(II) complexes of bis(acetylacetonatoethylenediamine) or Salen can be anchored to a polymer. Such complexes act as reversible oxygen carriers even at room temparature[100]. The oxygenations in these cases can be monitored by either ESR or visible spectroscopy.

Also there are some reports of zeolite encapsulated Schiff base complexes acting as oxidation catalysts recently. Co-salen has been synthesised within the supercage of zeolite X. The catalyst is stable during the catalytic cycle and no leaching out of the ligand occurs during oxidation[101].

The major problem associated with the study of catalytic process is the lack of information about the intermediates or of the active catalyst. a method has been developed by Gassman et al [102] for the isolation and characterisation of highly reactive intermediates in homogenious catalysis by transition metal complexes. The method involves the principle of steric exclusion type chromatography, which has been devised for the isolation of highly reactive intermediate on the surface of a porous polymer film. Analysis of these surface isolated intermediates was carried out by X-ray photoelectron spectroscopy which provide detailed information about the complexes that recided on the surface of the film.

Scope of the Present Investigation

Literature survey revealed that, there is not much work on the Schiff base complexes derived from quinoxaline-2-carboxaldehyde. The two nitrogen atoms present in the quinoxaline ring may affect, to certain extent, the electronic properties of the complexes. These effects can be well reflected in the electron transfer processes involved in catalysis. Hence we undertook this work with the following objectives:

1. To synthesise some new Schiff base ligands derived from the heterocyclic aldehyde, quinoxaline-2-carboxaldehyde.
2. To investigate the structure of some new metal complexes of such Schiff bases.
3. To study the catalytic activity of the synthesised complexes in the oxidation of ascorbic acid to dehydroascorbic acid.
4. To investigate the mechanism of catalysis by the synthesised complexes.

The ligands chosen for the present study are the following:

1) quinoxaline-2-carboxalidene-2-aminophenol(QAP)

2) quinoxaline-2-carboxaldehyde semicarbazone(QSC)

3) quinoxaline-2-carboxalidene-o-phenylenediamine(QOD)

4) quinoxaline-2-carboxalidene-2-furfurylamine(QFA)

Manganese(II), iron(III), cobalt(II), nickel(II) and copper(II) complexes of these Schiff have been synthesised and characterised. The synthesised complexes have been screened for their catalytic activity in the oxidation of ascorbic acid to dehydroascorbic acid. The mechanism of catalysis by the copper(II) complex of quinoxaline-2-carboxalidene-2-aminophenol has been studied in detail.

REFERENCES

1. B. O. West, Rev. Pure Appl. Chem. (Australia), 10 (1960) 207.

2. A. D. Garnovski, A. L. Nivoroshkin and V. I. Minkin, Coord. Chem. Rev., 126 (1993) 1.

3. M. Calligaris, G. Nardin and L. Randaccio, Coord. Chem. Rev. 7 (1972) 385.

4. A. E. Martell and M. Calvin, Chemistry of the metal ahelate compounds, Prentice Hall, Englewood Cliffs, N. J. (1959).

5. S. Yamada, Coord. Chem. Rev., 1 (1966) 415.

6. N. Matsumoto, T. Hara, A. Hirana and O. Hyoshi, Bull. Chem. Soc. Jpn., 56 (1983) 275.

7. R. K. Sharma and J. P. Tandon Indian J. Chem. 19A (1980) 376.

8. J. Gomez Lara, A. A. Sanchez, Spectrochim. Acta Part A, 23 (1967) 1299.

9. R. H. Holm, G. W. Everett and A. Chakravortty, Progr. Inorg. Chem. 7 (1966) 83.

10. O. West,"The chemistry of coordination compounds of Schiff bases New Pathways in Inorganic Chemistry", eds. E. A. Vebswor, A. G. Maddock and A. G. Sharpe, Cambridge University Press (1988).

11. S. G. Pine and B. dikic, J. Org. Chem., 55 (1990) 1932.

12. Gawinecki, Pol.J. Chem., 60 (1987) 831.

13. L. Carbonaro, A. Gacomelli, L. Senatore and L. Valli, Inorg. Chim. Acta, 165 (1989) 19.

14. D. H. Brown, J. H. Morris, G. Oates and W. Smith, Spectrochim. Acta Part A, 38 (1983).

15. R. Butcher and E. Sinn, Inorg Chem., 15 (1976) 1604.

16. D. H. Busch, Rec. Chem. Progr., 25 (1964) 107.

17. L. F. Lindoy and S. E. Livingstone, Inorg. Chim. Acta, 1 (1967) 365.

18. T. Ho and N. Tanaka, J. Inorg. Nucl. Chem., 32 (1970) 155.

19. J. Costamagna, J. Vargas, R. Latorre and G. Mena, Coord. Chem. Rev., 67 (1992) 119.

20. L. F. Lindoy, Coord. Chem. Rev., 4 (1969) 41.

21. E. G. Vassian and R. K. Murmann, Inorg. Chem., 6 (1967) 2043.

22. E. J. Olszewski and D. F. martin, J. Inorg. Nucl. Chem. , 26 (1964) 1577.

23. E. J. Olszewski and D. F. martin, J. Inorg. Nucl. Chem. , 27 (1965) 345.

24. H. S. Verter and A. E. Frost, J. Am. Chem. Soc., 82 (1960) 85.

25. D. F. Martin, Adv. Chem. Series 37 (1963) 192.

26. Y. Muto, Bull. Chem. Soc. Japan, 33 (1960) 1242.

27. D. H. Busch, Rec. Chem. Progr., 25 (1964) 107; L. F. Lindoy and D. H. Busch, "Metal Complexes of Macrocyclic Ligands", in "Preparative Inorganic Reactions", ed. W. L. Joby, Wiley-Interscienc, New York, 6 (1971).

28. A. W. Struss and D. F. Martin, J. Inorg. Nucl. Chem., (1963) 1409.

29. R. G. Cozens, K. S. Murray and B. O. West, Aust. J. Chem., 23 (1970) 683.

30. H. Schiff, Annalen, 150 (1869) 193.

31. J. Costamagna, J. Vargas, R. Latorre and G. Mena, Coord. Chem. Rev., 119 (1992) 67.

32. W. Klemm and R. H. Raddetz, Z. Anorg. Allgem. Chem., 250 (1942) 207.

33. C. Sheringer, K. Hinkler and M. V. Stackelberg Z. Anorg. Allgem. Chem., 35 (1966) 306.

34. M. Gerloch, J. Lewis, F. E. Mabbs and A. Richards, Nature, 212 (1966) 809.

35. M. Gerloch and F. E. Mabbs, J. Chem. Soc., A (1967) 1958.

36. S. N. Poddar, and K. Dey, Z. Anorg. Allgem. Chem., 327 (1964) 104.

37. J. B. Wills and D. P. Mellor, J. Am. Chem. Soc., 69 (1947) 1237.

38. V. I. Minkin, O. A. Osipov, V. A. Kogan, K. R. Seragidullin, R. L. Terent'ev and O. A. Roevskii, Russ. J. Phys. Chem., 38 (1964) 938.

39. J. Vargas, L. Araya and J. Costamagna, Bol. Soc. Chil. Quim.,

33 (1988) 13.

40. J. Canales, J. Vargas, G. Mena and J. Costamagna, Proc. Cong. Latinoam. Quim. (FLAQ), 18 (1988) 621.

41. G. Dudek and E. P. Dudek, J. Chem. Soc. B (1971) 1356.

42. A. R. Hendrickson,J. M. Hope and R. L. Martin, J. Chem. Soc. Dalton Trans., (1979) 1497.

43. N. Bresciani-Pahor, M. Calligaris, P. Delise, G. Dodic, G. Nardin and L. Randaccio, J. Chem. Soc.Dalton Trans. (1976) 2478.

44. V. K. Kravtsov et al, J. Coord. Chem., 7 (1981) 776.

45. J. Costamagna, Contrib. Cient. Tecnol. (USACH), 87 (1988).

46. C. Srivanavit and D. G. Brown, J. Am. Chem. Soc., 100 (1978) 5777.

47. R. H. Holm and E. H. Abott, in A. E. Martell(Ed.), Coordination Chemistry, American Chemical Society Monograph, 1975

48. P. R. Blum, R. M. C. Wel and S. C. Cummings, Inorg. Chem., 13 (1974) 450.

49. I. Bertini, L. Sacconi and G. P. Speroni, Inorg. Chem., 11 (1972) 1323.

50. R. H. Holm, A. Chakravorty and G. O. Dudek, J. Am. Chem. Soc., 85 (1964) 379, 3109.

51. A. Chakravorty and R. H. Holm, Inorg. Chem., 3 (1964) 1010.

52. V. Gutmann and R. Schmid, Coord. Chem. Rev., 12 (1974) 263.

53. N. Sadasivan, J. E. Endicott, J. Am. Chem. Soc. 88 (1966) 5468.

54. J. Csaszar, Acta. Phys. Chem.Szeged, 28 (1982) 35, 45, 59.

55. A. B. P. Lever, Inorganic Electronic Spectroscopy, Elsevier Amsterdam, 2nd Edn. 1988.

56. P. Gluvchinsky and G. Mockler, Spectrochim. Acta, 33 (1977) 1077.

57. J.Csaszar and J. Balog, Acta. Chim. Acad. Sci. Hung., 87 (1975) 331.

58. B. D. Sharma and J. C. Bailer, Jr., J. Am. Chem. Soc., 77 (1955) 5476.

59. B. D. Sharma, K. R. Ray, R.E. Sievers and J. C. Bailer, Jr., J. Am. Chem. Soc., 86 (1964) 14.

60. C. F. Bell, K. A. K. Lott and N. Hearn, Polyhedron, 6 (1987) 39.

61. L. F. Lindoy and S. E. Livingstone; Inorg. Chim; Inorg. Chim. Acta, 1 (1967) 1149.

62. B. Kirson and S. YarivB. Kirsonand S. Yariv, Bull. Soc. Chim. France, (1964) 2969; 1565, 149.

63. H. Masaaki and K. Kyoko, Inorg. Chim. Acta, 104 (1985) 47.

64. C. T. Spencer and L. T. Tailor, Inorg. Chem., 12 (1973) 644.

65. B. Kuncheria, G. Devi and P. Indrasenan, Inorg. Chim. Acta, 155 (1989) 255

66. F. P. Dwyer, N. S. Gill, E. C. Gyarfas and F. Lions, J. Am. Chem. Soc., 79 (1957) 1269.

67. F. Lions and K. V. Martin, J. Am. Chem. Soc, 79 (1957) 1572.

68. H. K. Parwana and G. Singh, Indian J. Chem 26A (1987) 581

69. E. W. Ainscough, A. M. Brodie, J. D. Ranford and J. M. Watwers, J. Chem. Soc., (1991) 2125.

70. J. G. Tojal, M. K. Urtiaga, R. Cortes, L. Lezama, T.Rojo and M. I. Arriortua, J. Chem. Soc. Dalton Trans., (1994) 2233.

71. E. W. Ainscough, A. M. Brodie, J. D. Ranford and J. M. Waters J. Chem. Soc., Dalton Trans., (1991) 1737).

72. E. W. Ainscough, A. M. Brodie, J. D. Ranford, J. M. Waters and K. S. Murray, Inorg. Chim. Acta, 197 (1992) 107

73. J. G. Tojal, J. G. Jaca, R. Cortes, T. Rojo, M. K. Urtiaga and M. I. Arriortua, Inorg. Chim. Acta, 249 (1996) 25.

74. H. Beraldo and L. Tosi, Inorg. Chim. Acta, 125 (1986) 173.

75. R. W. Brockman, J. R. Thompson, M. J. Bell and H. E. Skipper, Cancer Res. , 16 (1956) 167.

76. W. E. Antholine, P. Gunn and L. E. Hopwood, Int. J. Radiat. Oncology, Biol. Phys. 7 (1981) 491.

77. L. A. Saryan, K. Mailer, C. Krishnamurthy, W. Antholine and D. H. Petering, Biochem. Pharmacol., 30 (1981) 1595.

78. G. W. Bushnell and A. Y. M. Tasang, Can. J. Chem., 57 (1979) 603.

79. A. R. Karthikeyan, Ph.D. Thesis, Cochin University of Science and Technology, Kochi, Kerala, India (1992).

80. K. K. M. Yusuff and R. Sreekala, Synth. React. Inorg. Met. -Org. Chem., 21 (1991) 575.

81. R. Sreekala and K. K. M. Yusuff, Synth. React. Inorg. Met. -Org. Chem., 24 (1994) 1773.

82. Jose Mathew, Ph.D. Thesis, Cochin University of Science and Technology, Kochi, Kerala, India (1995).

83. S. G. Valavi, Ph.D. Thesis, Cochin University of Science and Technology, Kochi, Kerala, India (1995).

84. N. Kitajima, H. Fukui and Y. Moro-oka, J. Chem. Soc. Chem. Commun., (1988) 485.

85. J. C. Bailer, Catal. Rev. Sci. Eng., 10 (1974) 17.

86. M. M. Taqui Khan, and A. E. Martell, "Homogeneous Catalysis by Metal Complexes", Academic Press, New York (1981)

87. I. Sasaki, D.Pujol and A. Goudemer, Inorg. Chim. Acta, 134 (1987) 53.

88. M. Nath, Kamaluddin, J. Cheema, Indian J. Chem. 32A (1993)108.

89. W. Zhang, J. L. Loebach, S. R. Wilson and E. N. Jacobson, J. Am. Chem. Soc., 112 (1990) 2801; R. Irie, K. Noda, Y. Ito, N. Matsumoto and T. Katsuki, Tetrahedron Lett. 31 (1990) 7345.

90. H. Yoon and C. J. Burrows, J. Am. Chem. Soc., 110 (1988) 4087;
W. Zhang and E. N. Jacobson, J. Org. Chem., 56 (1991) 2296.

91. T. Schwenkreis and A. Berkessel, Tetrahedron Lett., 34 (1993) 4785.

92. T. Nagata, K. Imagawa, T. Yamada and Mukaiyama, Chem. Lett., (1994) 1259

93. P. K. Bhattacharya, Proc. Indian Acad. Sci., 102 (1990) 247.

94. A. S. Hay, Encycl. Polym. Sci. Technol. 10 (1969) 92.

95. F. Bosolo, R. D. Jones, D. A. Summerville, Chem. Rev. 79 (1979)

96. T. Tsumaki, Bull. Chem. Soc. Jpn., 13 (1938) 252.

97. R. H. Bailes and M. Calvin, J. Am. Chem. Soc., 69 (1946) 1886.

98. A. E. Martell and Y. Sun, Inorg. Chem., 28 (1989) 2649.

99. Y. Abe, K. Shinguhara and S. Yano, Chem. Lett., (1992) 897.

100. E. Tsuchida and H. Nishida., Adv. Polymer Sci, 24 (1977) 1.

101. C. Ratnasamy, A. Murugkar and S. Padhye, Indian J. Chem., 35A (1996) 1.

102. P. G. Gassman, D. W. Macomber and S. M. Willging, J. Am. Chem. Soc., 107 (1985) 2380.

CHAPTER II
EXPERIMENTAL TECHNIQUES

2.1 INTRODUCTION

Details about the general reagents used, preparation of ligands and various analytical and physico-chemical methods employed for the characterisation of the metal complexes are discussed in this chapter. Procedural details regarding the synthesis of metal complexes are given in the appropriate chapters.

2.2 REAGENTS

The following metal salts were used: $MnCl_2.4H_2O$ (E.Merck), $FeCl_3$ (Aldrich, 98% pure), $CoCl_2.6H_2O$ (E. Merck), $NiCl_2.6H_2O$ (BDH), $CuCl_2.2H_2O$ (E. Merck) $Mn(CH_3COO)_2.4H_2O$ (Merck), $Co(CH_3COO)_2.4H_2O$ (Merck), $Ni(CH_3COO)_2.4H_2O$ (Merck) and $Cu(CH_3COO)_2.H_2O$ (Merck). 2-Aminophenol (Merck), semicarbazide hydrochloride (BDH), *o*-phenylene diamine (Merck) and 2-furfuryl amine (Merck) were also used for the present work. Unless otherwise specified, all other reagents were either of 99% purity or purified by known laboratory procedures[1].

2.3 PREPARATION OF QUINOXALINE-2-CARBOXALDEHYDE

A procedure reported by Ohle et al was used to synthesise quinoxaline-2-carboxaldehyde[2,3](Fig. 2.1).

Treatment of D-glucose with o-phenylenediamine in the presence of hydrazine hydrate and acetic acid on a boiling water bath under carbon dioxide atmosphere provided by the addition of a pinch of sodium bicarbonate, gave the compound 2-(D-arabinotetrahydroxybutyl) quinoxaline. Synthesis of quinoxaline-2-carboxaldehyde was carried out by the oxidation of this compound with sodium metaperiodate in water in the presence of acetic acid at laboratory temperature. The product was isolated by extraction with ether and purified by recrystallisation from petroleum ether.

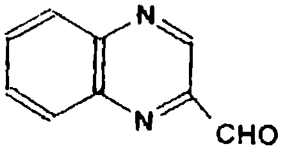


Fig. 2.1 Strcture of quinoxaline-2-carboxaldehyde

2.4 PREPARATION OF LIGANDS

2.4.1 *Quinoxaline-2-carboxalidene-2-aminophenol (HQAP)*

The ligand (HQAP) was prepared by mixing an ethanolic solution (100 mL) of quinoxaline-2-carboxaldehyde (0.01 mol; 1.58 g) and 2-aminophenol (0.01 mol; 1.09 g) in ethanol (100 mL). The solution was refluxed for 1 h. The ligand separated out was filtered and dried *in vacuo* over anhydrous calcium chloride. (Yield: 70%, 1.7 g, M.P.: 225^{0}C).

2.4.2 *Quinoxaline-2-carboxaldehyde semicarbazone (QSC)*

The ligand (QSC) was prepared by mixing an ethanolic solution (100 mL) of quinoxaline-2-carboxaldehyde (0.01 mol; 1.58 g) and semicarbazide hydrochloride (0.01 mol; 1.11 g) in ethanol (100 mL). The solution was stirred for fifteen minutes. The ligand separated out was filtered and washed with ethanol. It is then dried *in vacuo* over anhydrous calcium chloride. (Yield: 62%, 1.55 g, M.P.: 230°C).

2.4.3 *Quinoxaline-2-carboxalidene-o-phenylenediamine (QOD)*

To prepare the ligand QOD, an ethanolic solution (100 mL) of quinoxaline-2-carboxaldehyde (0.01 mol; 1.58 g) was mixed with o-phenylenediamine (0.01 mol; 0.54 g) in ethanol (100 mL). The resultant solution was stirred for fifteen minutes. The orange coloured ligand separated was filtered and washed with ethanol and dried *in vacuo* over anhydrous calcium chloride. (Yield: 70%, 1.62 g, M.P.: >230°C)

2.4.4 *Quinoxaline-2-carboxalidene-2-furfurylamine (QFA)*

The ligand QFA was prepared by mixing a solution (50 mL) of quinoxaline-2-carboxaldehyde (0.01 mol; 1.58 g) in 1,2-dichloromethane with furfurylamine (0.01 mol; 0.97 g; 0.88 mL) and refluxing the solution for fifteen minutes. This ligand solution was used as such for the preparation of the complexes.

2.5 ANALYTICAL METHODS

2.5.1 *Estimation of Metals*

In all the cases, the organic part of the complexes was completely eliminated before the estimation of metal ions. The following procedure was adopted for this purpose in the case of all the complexes. A known weight (0.2–0.3) of the metal complex was treated with concentrated sulphuric acid (5 mL) followed by concentrated nitric acid (20 mL). After the reaction had subsided, perchloric acid (5 mL, 60%) was added. This mixture was refluxed until the colour of the solution changes to that of the corresponding metal salt. The clear solution thus obtained was evaporated to dryness. After cooling, concentrated nitric acid (15 mL) was added and evaporated to dryness on a water bath. The residue was dissolved in water and this neutral solution was used for the estimation of metals.

Manganese was estimated complexometrically using EDTA. Iron was estimated by titrating against standard potassium dichromate solution after reducing to iron(II) with $SnCl_2$. Gravimetric procedures[4] were used for the estimation of cobalt and nickel. Cobalt was estimated by precipitating it as $[Co(C_5H_5N)_4](SCN)_2$ using ammonium thiocyanate and pyridine. Nickel was estimated as nickel dimethylglyoximate complex by adding an alcoholic solution of dimethylglyoxime followed by ammonia solution. Iodometric method was employed for the estimation of copper in the complexes.

2.5.2 *CHN Analysis*

Microanalyses for carbon, hydrogen and nitrogen were done on a Heraeus CHN elemental analyser. Analytical data are given in Table II.1.

2.5.3 *Estimation of halogen*

Halogen content was determined by peroxide fusion of the sample followed by volumetric estimation using Volhard's method.

2.6. PHYSICO-CHEMICAL METHODS

2.6.1. *Conductance Measurements*

Molar conductances of the complexes in nitrobenzene, methanol or acetonitrile were determined at 28 ± 2°C using a conductivity bridge (Century 601) with a dip type cell and a platinised platinum electrode.

2.6.2. *Magnetic Susceptibility Measurements*

The magnetic susceptibility measurements were done at room temperature (28 ± 2°C) on a simple Gouy-type magnetic balance. The Gouy tube was standardised using $Co[Hg(SCN)_4]$ as standard, as recommended by Figgis and Nyholm [5]. The effective magnetic moments were calculated using the equation,

$$\mu_{eff} = 2.84\ (\chi_m T)^{1/2}\ \text{B.M.}$$

where T is the absolute temperature and x_m is the molar susceptibility corrected for diamagnetism of all the atoms present in the complex using Pascal's constants[6-8].

Table II.1

Analytical Data of Ligands

Compound	C % Found (Calc.)	H % Found (Calc.)	N % Found (Calc.)
HQAP	73.07 (73.30)	4.35 (4.40)	16.79 (16.90)
QSC	56.20 (56.30)	4.15 (4.20)	32.81 (32.90)
QOD	71.89 (72.60)	4.63 (4.80)	22.33 (22.60)
QFA	70.27 (70.90)	4.44 (4.60)	17.46 (17.70)

2.6.3 *Electronic Spectra*

Electronic spectra were taken in solution or in the solid state by mull technique following a procedure recommended by Venanzi[9]. The procedure is as given below:

Small filter paper strips were impregnated with a paste of sample in nujol. These were placed over the entrance to the photocell housing. A nujol treated filter paper strip of similar size and shape was used as the blank. The electronic spectra of the complexes in the region 1000–200 nm were recorded on a Shimadzu UV-Vis 160A spectrophotometer.

The near IR spectra of complexes in the region 2000–1000 nm were recorded with a Hitachi U-3410 spectrophotometer.

2.6.4 *Infrared Spectra*

Infrared spectra of the ligands and the complexes in the region 400–4000 cm^{-1} were taken both as nujol paste and as KBr discs on a Shimadzu 8101 FTIR spectrophotometer.

2.6.5 *EPR Spectra*

The X-band EPR spectra of the copper(II) complexes were taken in chloroform-toluene mixture at room temperature using Varian E-112 X/Q band spectrophotometer.

REFERENCES

1. D. D. Perrin, W. L. F. Armarego and D. R. Perrin, "Purification of Laboratory Chemicals , Pergamon Press, Oxford (1980).

2. M. H. Ohle, Ber, 74B (1941) 13.

3. C. L. Leese and H. N. Rydon, J. Chem. Soc., (1955) 303.

4. A. I. Vogel, "A Text book of Quantitative Inorganic Analysis" , 4th Edn., ELBS Longman, England, (1978).

5. B. N. Figgis and R. S. Nyholm, J. Chem. Soc., (1958) 4190.

6. B. N. Figgis and J. Lewis, "Modern Coordination Chemistry", J. Lewis and R. G. Wilkins, Eds., Interscience, New York (1958).

7. P. W. Selwood, "Magnetochemistry" , Interscience, New York (1958).

8. B. N. Figgis and J. Lewis, "Progress in Inorganic Chemistry" , F. A. Cotton, Ed., Interscience, New York (1964).

9. G. Dyer, J. G. Hartley and L. M. Venanzi, J. Chem. Soc. (1965) 1293.

CHAPTER III

QUINOXALINE-2-CARBOXALIDENE-2-AMINOPHENOL COMPLEXES OF MANGANESE(II), IRON(III), COBALT(II), NICKEL(II) AND COPPER(II)

3.1 INTRODUCTION

Aminophenols are important in the pharmaceutical industry, since they have antibacterial and antitubercular action. Aminophenols condense with various aldehydes and ketones, which can form metal complexes of varying structural types[1,2]. Schiff bases obtained by the condensation of 2-aminophenol with some aldehydes and ketones have also been used widely as antituberculosis compounds and their biological action has been attributed to their ability to form metal chelates[3-5]. We have synthesised transition metal complexes of the Schiff base derived from quinoxaline-2-carboxaldehyde and 2-aminophenol (HQAP) and the results of our studies are presented in this chapter.

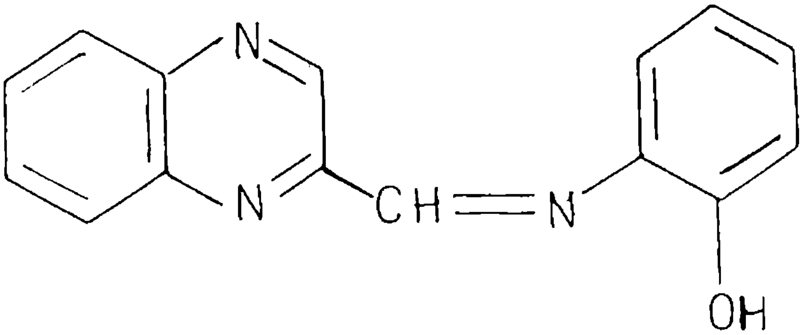


Fig. 3.1 Structure of HQAP

3.2 EXPERIMENTAL

3.2.1 *Materials*

The procedure for the preparation of quinoxaline-2-carboxalidene-2-aminophenol is given in Chapter II.

3.2.2 *Preparation of the Complexes*

The complexes of manganese(II), iron(III), cobalt(II), nickel(II) and copper(II) were prepared by the following general procedure:

An ethanolic solution of the Schiff base (HQAP) (0.01 mol; 2.49 g) (100 mL) was mixed with the corresponding metal salt solution in ethanol (0.005 mol; 1.22 g of $(CH_3COO)_2Mn.4H_2O$, 0.81 g of anhydrous $FeCl_3$, 1.25 g of $(CH_3COO)_2Co.4H_2O$, 1.24 g of $(CH_3COO)_2Ni.4H_2O$ or 0.99 g of $(CH_3COO)_2Cu.H_2O$). The solution was refluxed for 2 h. The volume of the resulting solution was then reduced by evaporation and the solution was cooled in a freezer for about 1 h. The crystalline complex separated out was filtered, washed with ether and dried *in vacuo* over anhydrous calcium chloride (Yield: 60-70%, M.P.:> 250 ^{0}C).

3.2.3 *Analytical Methods*

The techniques employed for the characterisation of metal complexes are given in Chapter II.

3.3 RESULTS AND DISCUSSION

The complexes are found to be stable in air and non-hygroscopic. They are soluble in methanol, ethanol, chloroform, acetonitrile, nitrobenzene, DMF and DMSO. The analytical data (Table III.1) show that these complexes have the general empirical formula, $[M(QAP)_2]$, except in the case of the iron(III) complex. The formula of the iron(III) complex is $[Fe(QAP)_2Cl]_2$. The very low molar conductance values of the complexes in methanol and nitrobenzene indicate the non-electrolytic nature of the complexes[6].

3.3.1 *Magnetic Susceptibility Measurements*

The magnetic moment values of the complexes are given in Table III.2. The magnetic moment value of 5.7 B.M. for the manganese(II) complex indicates the presence of five unpaired electrons and gives no specific information about its stereochemistry[7]. For the iron(III) complex the μ_{eff} value is observed to be 5.3 B.M. It appears to be less than that expected for spin-free octahedral complexes, indicating a bridged structure for this complex where antiferromagnetic coupling is operative[8-10]. For cobalt(II) and nickel(II) complexes the μ_{eff} values are 4.5 B.M. and 3.5 B.M. respectively and are in agreement with a tetrahedral structure[11-13]. The magnetic moment value of 2.2 B.M. observed for the copper(II) complex indicates a distorted tetrahedral structure[14].

Table III.1

Physical and Analytical Data

Complex . Mol.formula	Yield (%)	C (%) Found (Calc.)	H (%) Found (Calc.)	N (%) Found (Calc.)	M (%) Found (Calc.)	Cl (%) Found (Calc.)
$[Mn(QAP)_2]$	60	61.47 (61.72)	4.28 (4.51)	14.14 (14.60)	9.45 (9.94)	---
$[Fe(QAP)_2Cl]_2$	64	51.19 (51.88)	3.45 (3.78)	11.74 (12.04)	8.90 (9.01)	6.40 (6.42)
$[Co(QAP)_2]$	67	62.96 (63.54)	4.48 (4.99)	14.80 (14.96)	10.38 (10.58)	---
$[Ni(QAP)_2]$	64	64.37 (64.87)	4.22 (4.80)	15.42 (15.95)	8.92 (8.92)	---
$[Cu(QAP)_2]$	65	52.28 (52.61)	3.24 (3.56)	12.17 (12.85)	9.98 (10.35)	---

Table III.2

Magnetic and Conductance Data

Complex	Colour	Molar Conductance ($ohm^{-1}cm^{2}mol^{-1}$)	Magnetic Moment (B.M)
$[Mn(QAP)_2]$	Purple	0.1	5.7
$[Fe(QAP)_2Cl]_2$	Black	8.3	5.3
$[Co(QAP)_2]$	Purple	0.1	4.5
$[Ni(QAP)_2]$	Violet	0.1	3.5
$[Cu(QAP)_2]$	Brown	0.4	2.2

3.3.2 *Infrared Spectra*

The infrared spectral bands and the assignments of relevant bands are given in Table. III.3.

The infrared spectral data show that HQAP acts as a bidentate ligand and it coordinates through the phenolic oxygen and azomethine nitrogen atoms. Most of the bands due to the free ligand are present in the spectra of the complexes. The strong OH stretching band at 3500 cm^{-1} of HQAP is absent in the spectra of the complexes, which suggests that the phenolic oxygen atom is coordinated to the metal atom in the ionised form. The coordination of the phenolic oxygen atom in all the complexes is further supported by the fact that the strong band observed at 1282 cm^{-1} in the spectrum of the ligand, which is attributed to the phenolic C–O stretching vibration, undergoes a shift to higher wave numbers ($\Delta\nu$ = 20 cm^{-1}) in the spectra of the complexes[15,16]. The ν(C=N) band of the azomethine linkage appears at 1700 cm^{-1} in the spectrum of the ligand. This band is shifted to 1640–1645 cm^{-1} in the spectra of the complexes, indicating that the azomethine nitrogen is involved in complexation[17].

3.3.3 *Electronic Spectra*

The electronic spectra of all the complexes were recorded in methanol. The observed bands and their assignments are given in Table III.4. Most of the bands due to the free ligand are present in the spectra of the complexes.

Table III.3

Infrared Spectral Data

L	I	II	III	IV	V	Assignments
3500(s)	——	——	——	——	——	ν(O-H)
1700(s)	1645(s)	1640(s)	1645(s)	1640(s)	1640(s)	ν(C=N) azomethine
1579(w)	1578(w)	1578(w)	1578(w)	1580(w)	1580(w)	ν(C=N) ring
1490(s)	1490(s)	1490(s)	1490(s)	1490(s)	1495(s)	
1460(m)	1460(w)	1460(m)	1460(m)	1460(m)	1460(s)	
1380(sh)	1380(m)	1380(s)	1380(s)	1380(s)	1380(w)	
1360(m)	1360(m)	1360(sh)	1360(m)	1360(m)	1360(w)	
1330(m)	1340(sh)	1335(m)	1340(sh)	1340(w)	1335(w)	
1282(m)	1296(m)	1300(w)	1294(m)	1290(m)	1300(m)	ν(C=O)
1250(w)	1250(w)	1245(w)	1255(w)	1250(w)	1250(w)	
1210(w)	1210(w)	1210(m)	1210(m)	1210(w)	1210(w)	
1142(m)	1142(m)	1142(w)	1142(m)	1142(w)	1145(w)	
1122(m)	1122(m)	1122(m)	1122(m)	1122(m)	1122(m)	
1073(m)	1070(m)	1070(w)	1073(m)	1073(m)	1069(m)	
1010(s)	1010(s)	1010(s)	1010(s)	1010(s)	1010(s)	
980(w)	980(w)	980(w)	985(w)	985(w)	985(m)	
882(m)	880(w)	880(w)	880(w)	880(w)	880(w)	ρ(CH)
867(w)	867(w)	867(w)	862(w)	866(w)	866(w)	
760(s)	760(s)	760(s)	760(s)	760(s)	755(s)	ρ(CH)Ph
—	600(m)	600(s)	600(s)	600(s)	595(m)	ν(M-N)
490(w)	490(sh)	490(sh)	490(w)	490(w)	495(w)	
—	410(m)	410(m)	410(m)	410(w)	410(w)	ν(M-O)

Abbreviations:- s = strong, m = medium, w=weak and sh = shoulder

L = QAP, I = [Mn(QAP)$_2$], II = [Fe(QAP)$_2$Cl], III = [Co(QAP)$_2$],

IV = [Ni(QAP)$_2$], V = [Cu(QAP)$_2$]

Table III.4

Electronic Spectral Data of the Complexes

Compound	Abs. Max (cm^{-1})	log ε	Tentative Assignments
$[Mn(QAP)_2]$	47500	4.40	Intraligand transition
	40430	4.20	Intraligand transition
	28790	3.45	Charge transfer transition
	18270	1.28	$^6A_1 \longrightarrow {}^4T_1(G)$
$[Fe(QAP)_2Cl]$	47505	4.54	Intraligand transition
	42220	4.30	Intraligand transition
	31400	3.25	Charge transfer transition
$[Co(QAP)_2]$	46340	4.35	Intraligand transition
	40430	4.15	Intraligand transition
	27940	3.12	Charge transfer transition
	18630	1.34	$^4A_2 \longrightarrow {}^4T_1(P)$
	6250	0.95	$^4A_2 \longrightarrow {}^4T_1(F)$
$[Ni(QAP)_2]$	47500	4.41	Intraligand transition
	39580	4.12	Intraligand transition
	27940	3.10	Charge transfer transition
	17120	1.28	$^3T_1(F) \longrightarrow {}^3T_1(P)$
	5150	0.98	$^3T_1(F) \longrightarrow {}^3A_2(F)$
$[Cu(QAP)_2]$	46910	4.38	Intraligand transition
	40860	4.26	Intraligand transition
	31670	3.28	Charge transfer transition
	16600	1.17	d-d transition

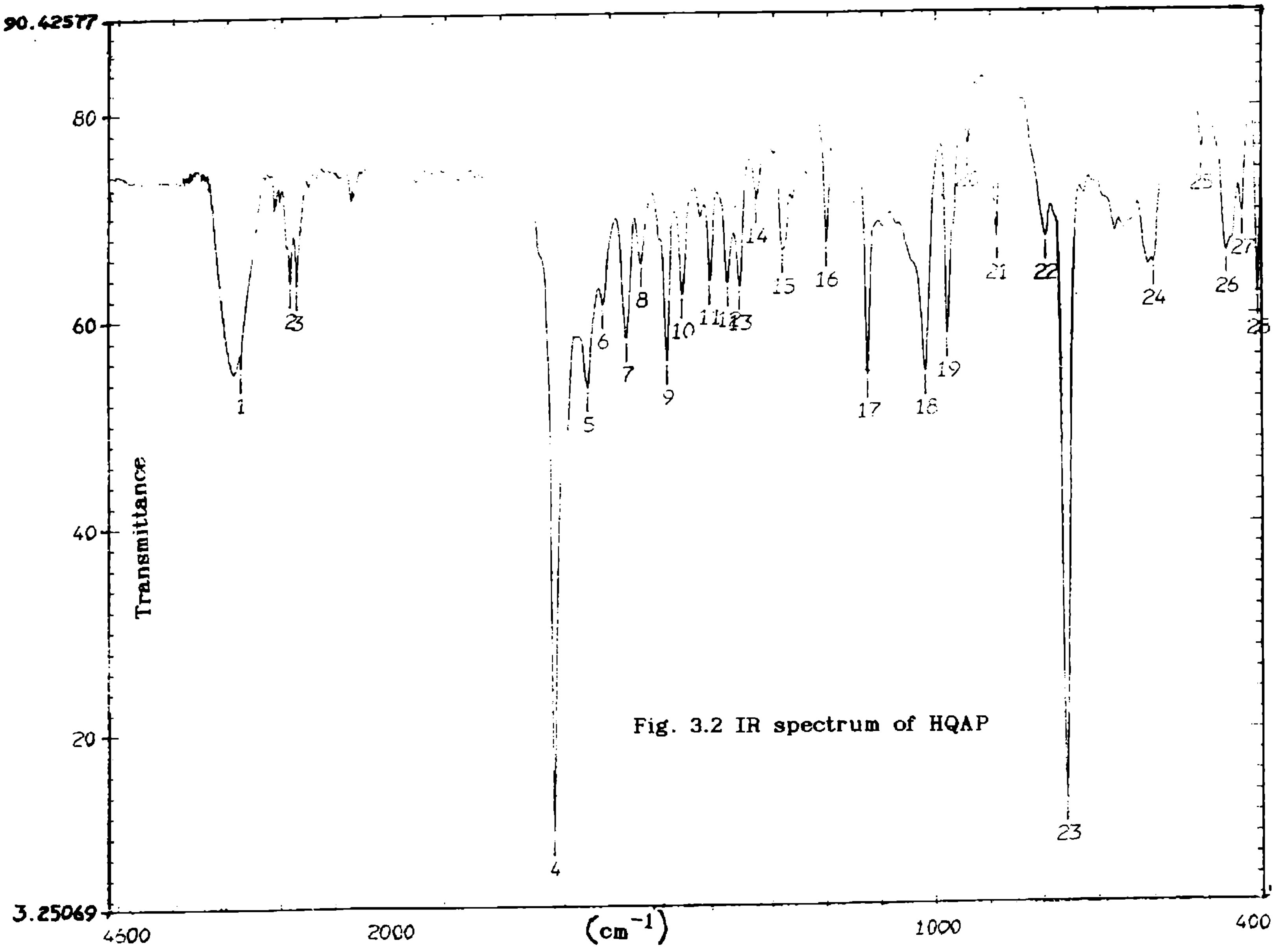


Fig. 3.2 IR spectrum of HQAP

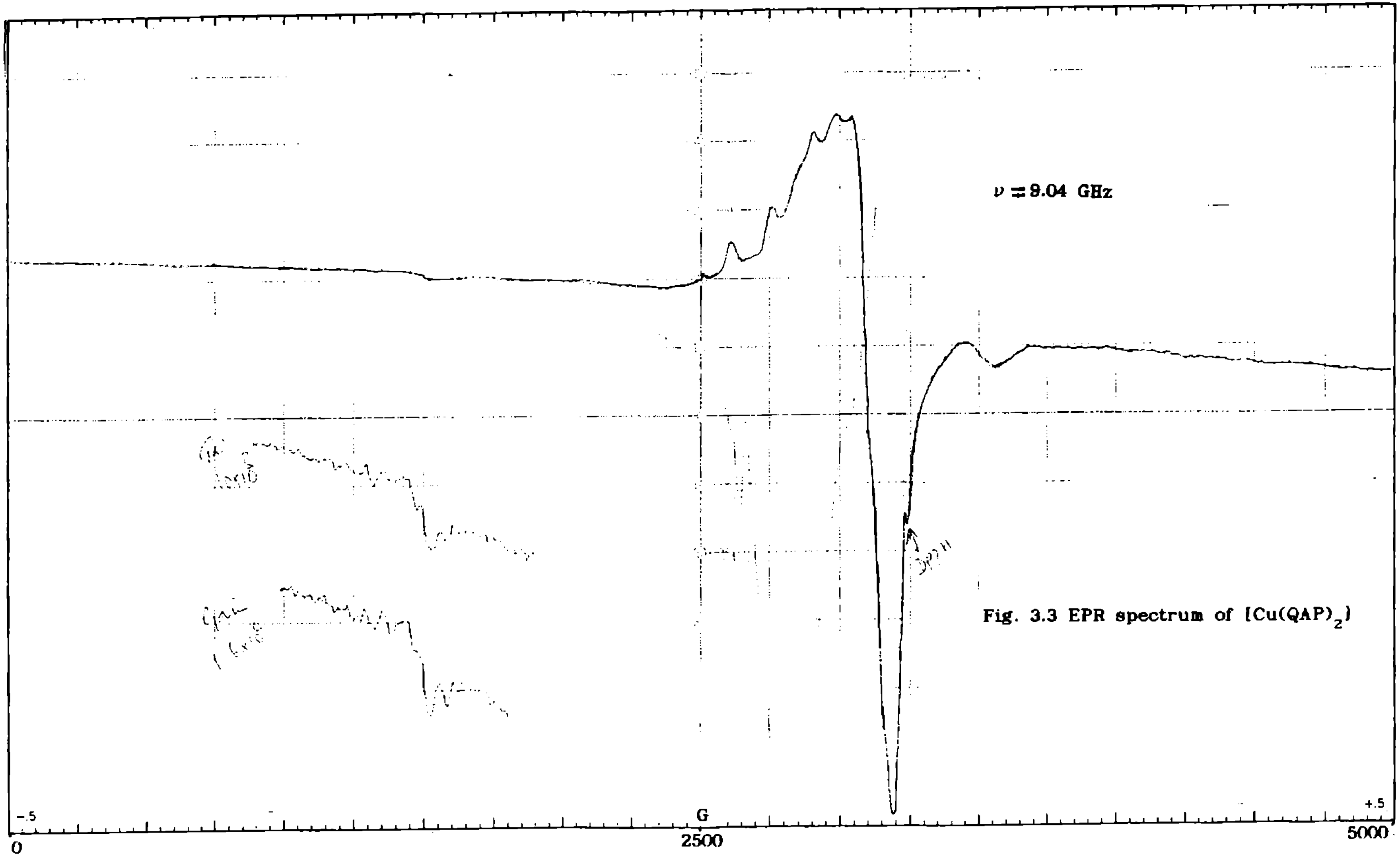


Fig. 3.3 EPR spectrum of $[Cu(QAP)_2]$

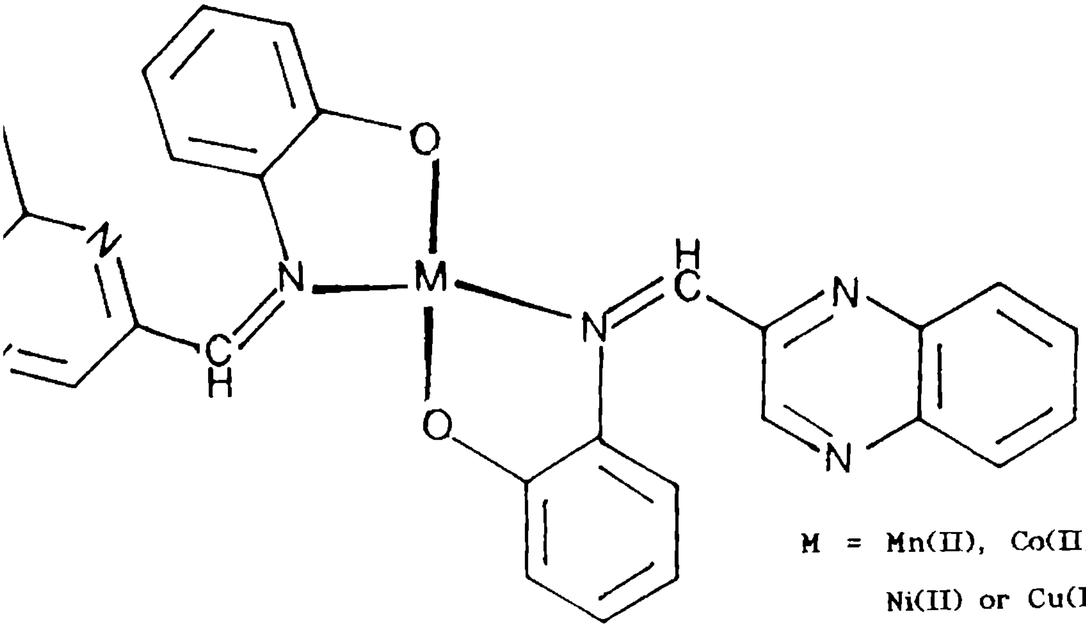
In the electronic spectra of all the complexes, broad bands are observed around 28000 cm^{-1} which can be assigned to charge transfer transitions. The absorptions observed around 40000 cm^{-1} and 47000 cm^{-1} are due to electronic transitions within the ligand[18]. A weak transition is observed at 18270 cm^{-1} in the spectrum of the present manganese(II) complex. The electronic transitions from the $^6A_1$ ground state of manganese(II) to higher energy states are spin-forbidden. The weak band appearing at 18270 cm^{-1} in the electronic spectrum of the present complex is assignable to the transition, $^6A_1 \longrightarrow {}^4T_1(G)$ and is indicative of a tetrahedral geometry[19-21] for manganese(II) ion. In the spectrum of the iron(III) complex, no bands were observed in the visible region.

The bands appearing at 18630 cm^{-1} and 6250 cm^{-1} in the spectrum of the cobalt(II) complex can be assigned to the transitions, $^4A_2 \longrightarrow {}^4T_1(P)$ and $^4A_2 \longrightarrow {}^4T_1(F)$ respectively which are typical of tetrahedral cobalt(II) complexes[22-24]. For the nickel(II) complex, the bands occurring at 17120 cm^{-1} and 5150 cm^{-1} are assigned to the $^3T_1(F) \longrightarrow {}^3T_1(P)$ and $^3T_1(F) \longrightarrow {}^3A_2(F)$ transitions respectively due to the tetrahedral structure around nickel(II)[22]. For the copper(II) complex, a broad d-d band is observed in the region 16600 cm^{-1}. A band around this region has been reported for copper(II) complexes with distorted tetrahedral structures[25].

3.3.4 *EPR Spectra*

The EPR spectrum (Fig.3.3) of $[Cu(QAP)_2]$ was recorded in ethanol at liquid nitrogen temperature. Kneubuhl's procedure[26] was used to calculate the g values. The g values and A value (g_1 = 1.81, g_2 = 2.07 and g_3 = 2.26; A = 144 G) observed for the present copper(II) complex show that the complex has a distorted tetrahedral stereochemistry[27].

Based on the above physico-chemical studies, the structures shown in Figures 3.4 and 3.5 may be assigned to the complexes.



M = Mn(II), Co(II), Ni(II) or Cu(II)

Fig. 3.4 Schematic structure of the complexes

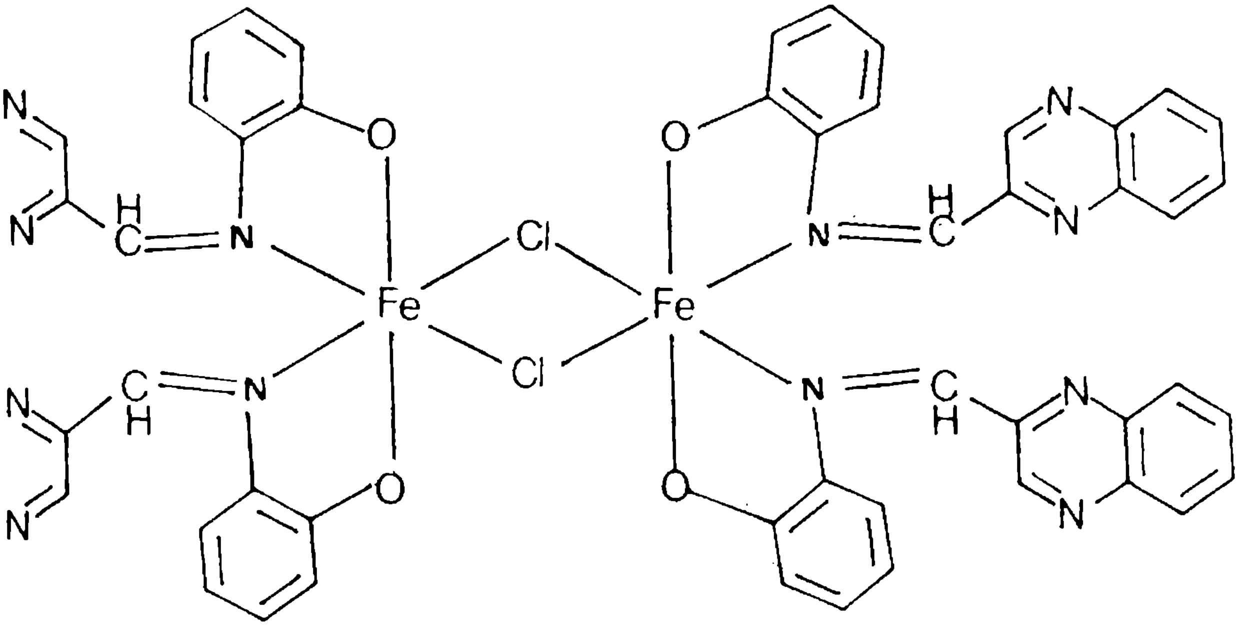


Fig. 3.5 Schematic structure of $[Fe(QAP)_2Cl]_2$

REFERENCES

1. M. M. Aly and Z. H. Khalil, J. Inorg. Nucl. Chem., 42 (1980) 1261.

2 A. D. Garnovski, A. I. Nivorozhkin and V. I. Minkin, Coord. Chem. Rev., 126 (1993) 1.

3. A. El-Dissouky and A. Z. El-Sonbati, Transition Met. Chem., 11 (1986) 112.

4. A. El-Dissouky and A. Z. El-Sonbati, Synth. React. Inorg. Met.-Org. Chem., 16 (1986) 1035.

5. A. El-Dissouky, G. B. Mohammed and A. Z. El-Sonbati, Inorg. Chim. Acta, 74 (1983) 279.

6. W. J. Geary, Coord. Chem. Rev., 7 (1971) 81.

7. N. S. Gill and R. S. Nyholm, J. Chem. Soc, (1959) 3997.

8. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 5th Ed. Wiley-Interscience, Singapore (1988).

9. L. Mishra, M. K. Said, Indian J. Chem., 35A (1996) 304.

10. M. K. Das, K. Chaudhary, N. Roy and P. Sarkar, Transition Met. Chem., 15 (1990) 468.

11. B. N. Figgis and J. Lewis, "Progress in Inorganic Chemistry", F. A. Cotton, Ed., Interscience, New York, 4 (1964) 185 .

12. A. Syamal, Trans. Met. Chem., 3 (1978) 279.

13. A. Z. El-Sonbati and M. A. Diab, Synth. React. Inorg. Met.-Org. Chem., 19 (1989) 731.

14. R. H. Nyholm, A. Chakraworthy and L. J. Theriot, Inorg. Chem. 5 (1966) 625.

15. R. L. Dutta and B. R. Das, Indian J. Chem., 22A (1983) 207.

16. J. E. Kovacic, Spectrochim. Acta, 23A (1967) 183.

17. B. Samuel, R. Sanith, C. Summerford and K. Wade, J. Chem. Soc. A (1970) 2019.

18. R. M. Silverstein, G. C. Bassler and T. C. Morril, "Spectrometric Identification of Organic Compounds", John Wiley & sons, 4th Ed. (1981).

19. C. R. Chaudhary and K. C. Dash, Indian J. Chem., 17A (1979) 364.

20. W. Kwoka, R. O. Moyer Jr. and R. Lindsay, J. Inorg. Nucl. Chem., 37 (1975) 1889.

21. K. S. Siddiqui, M. A. A. Shah and S. A. A. Zaidi, Indian J. Chem., 22A (1983) 812.

22. A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, New York, 2nd Edn. (1984).

23. N. Nawar, M. A. Khattab, M. M. Bekheit and A. H. Kaddah, Indian J. Chem., 35A (1996) 308.

24. D. L. Williams, D. W. Smith and R. C. Stouter, Inorg. Chem., 6 (1967) 590.

25. J. Gazo, L. B. Bersuker, J. Garaj, M. Kabesova, J. Kohout, K. Langfelderova, M. Melnik, M. Serator and F. Valach, Coord. Chem. Rev., 19 (1976) 253.

26. F. K. Kneubuhl, J. Chem. Phys., 33 (1960) 1074.

27. R. C. Rosenberg, C. A. Root, P. K. Bernstein and H. B. Gray, J. Am. Chem. Soc., 97 (1975) 2092.

CHAPTER IV

QUINOXALINE-2-CARBOXALDEHYDE SEMICARBAZONE COMPLEXES OF MANGANESE(II), IRON(III), COBALT(II), NICKEL(II) and COPPER(II)

4.1 INTRODUCTION

Semicarbazones are amongst the most important nitrogen-oxygen donor ligands[1]. These ligands are capable of acting as neutral or charged ligand moieties. During the past few years, a number of references describing the transition metal complexes of these ligands have appeared in the literature[2-4]. This chapter describes the synthesis and characterisation of quinoxaline-2-carboxaldehyde semicarbazone (QSC) complexes of manganese(II), iron(III), cobalt(II), nickel(II) and copper(II).

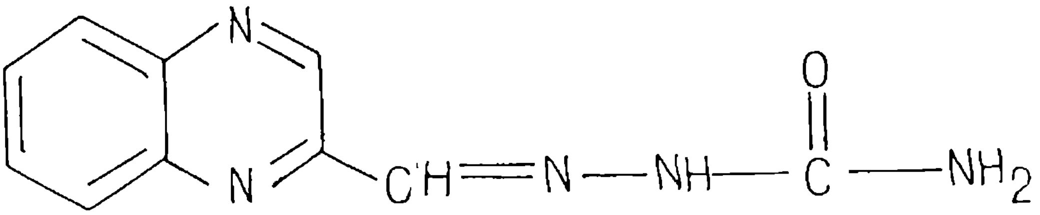


Fig. 4.1 Structure of QSC

4.2 EXPERIMENTAL

4.2.1 *Materials*

Details regarding the preparation and purification of the ligand are given in Chapter II.

4.2.2 *Synthesis of the Complexes*

All the complexes were prepared by the following general procedure. A solution of the ligand (0.02 mol; 4.3 g) in acetic acid was heated on a waterbath, and then mixed with a solution of the corresponding metal salt (0.01 mol; 1.98 g $MnCl_2.4H_2O$, 1.62 g $FeCl_3$, 2.37 g $CoCl_2.6H_2O$, 2.37 g $NiCl_2.6H_2O$ or 1.7 g $CuCl_2.2H_2O$). The complexes separated out on cooling were filtered, washed with chloroform and dried over anhydrous $CaCl_2$ (Yield: 60–70%; M.P.> 250^oC).

4.2.3 *Analytical Methods*

Details regarding the analytical methods employed and other characterisation techniques are given in Chapter II.

4.3 RESULTS AND DISCUSSION

The complexes isolated are non-hygroscopic amorphous powders and are stable in air. They are appreciably soluble in methanol, ethanol, acetonitrile, DMF and DMSO. The analytical data (Table IV.1) show that the complexes have the general formula $[M(QSC)Cl_2]$, except for the iron complex, in which case the formula is $[Fe(QSC)Cl_3]$. The molar conductance values show that these complexes are non-electrolytes in methanol.

4.3.1 *Magnetic Susceptibility Measurements*

The magnetic moment values of the complexes are shown in Table IV.2. The μ_{eff} value of 5.8 B.M. for the manganese(II) complex corresponds to the presence of five unpaired electrons and gives no

Table IV.1

Physical and Analytical data

Complex	Yield (%)	C(%) Found (Calc)	H(%) Found (Calc)	N(%) Found (Calc)	M(%) Found (Calc)	Cl(%) Found (Calc)
[Mn(QSC)Cl$_2$]	70	34.80	2.30	20.20	16.09	20.50
		(35.20)	(2.64)	(20.50)	(16.10)	(20.80)
[Fe(QSC)Cl$_3$]	65	31.60	2.33	18.30	14.40	27.80
		(31.80)	(2.40)	(18.60)	(14.80)	(28.20)
[Co(QSC)Cl$_2$]	70	34.50	2.50	19.90	16.80	19.50
		(34.80)	(2.60)	(20.30)	(17.10)	(20.60)
[Ni(QSC)Cl$_2$]	65	34.60	2.40	20.10	16.90	20.04
		(34.80)	(2.60)	(20.30)	(17.03)	(20.60)
[Cu(QSC)Cl$_2$]	70	33.90	2.30	19.80	17.70	19.80
		(34.30)	(2.60)	(20.03)	(18.20)	(20.30)

Table IV.2

Molar Conductance and Magnetic Moment Data

Complex	Colour	Molar Conductance (ohm^{-1} cm^{2} mol^{-1})	Magnetic Moment (B.M)
[Mn(QSC)Cl_2]	brownish yellow	19.2	5.8
[Fe(QSC)Cl_3]	black	6.4	5.6
[Co(QSC)Cl_2]	brownish yellow	13.0	4.5
[Ni(QSC)Cl_2]	brownish yellow	2.6	4.0
[Cu(QSC)Cl_2]	light brown	2.2	1.9

specific information about its stereochemistry[5]. For the iron(III) complex, the magnetic moment value is 5.6 B.M., which indicates the presence of high spin iron(III) structures. Magnetic moment values of 4.5 B.M. and 4.0 B.M. for the cobalt(II) and nickel(II) complexes are in agreement with a tetrahedral structure for these complexes[6]. The copper(II) complex exhibits a magnetic moment value of 1.9 B.M, which is close to the values reported in the case of many square planar complexes of copper(II)[7,8].

4.3.2 *Infrared Spectra*

The infrared spectral data (Table IV.3) show that QSC acts as a bidentate ligand, coordinating through azomethine nitrogen atom and ring nitrogen atom, except in the case of the iron(III) complex where it acts as a tridentate ligand, using the carbonyl oxygen atom in addition to the other two ligating atoms. The ligand exhibits a band around 1710 cm^{-1}, which might be assigned as a combination of $\nu(C=N)$ of the azomethine group and $\nu(C=O)$ of the semicarbazone. In the spectra of the complexes, $\nu(C=N)$ appears as a strong peak at 1670 cm^{-1}, which indicates the participation of the azomethine nitrogen in bonding to the metal atom[2]. A very weak band is retained at about 1710 cm^{-1} except for the iron complex, in which case this band completely disappears. This indicates that the carbonyl oxygen atom is taking part in complexation only in the case of the iron complex. The appearance of a medium intensity band at 491 cm^{-1} in the spectra of the iron(III) complex which may be assigned to $\nu(M-O)$ further evidences the coordination of the

Table IV.3

Infrared Spectral Data

L	I	II	III	IV	V	Assignment
3300(m)	3300(m)	3295(m)	3295(m)	3295(m)	3300(m)	ν(N-H)
3240(m)	3240(m)	3240(m)	3240(m)	3240(m)	3240(m)	
1710(s)	1708(w)	——	1710(w)	1708(w)	1708(w)	ν(C=O)
1710(s)	1676(s)	1672(s)	1677(s)	1678(s)	1680(s)	ν(C=N) azomethine
1613(w)	1613(w)	1614(w)	1613(w)	1609(w)	1613(w)	
1585(s)	1544(m)	1541(m)	1539(m)	1541(m)	1539(m)	ν(C=N) (ring)
1488(w)	1495(w)	1496(w)	1496(w)	1496(w)	1490(w)	
1400(m)	1398(m)	1403(m)	1400(m)	1400(m)	1385(m)	
1366(w)	1372(w)	1370(w)	1369(w)	1367(w)	1364(w)	
1171(m)	1168(m)	1170(m)	1174(m)	1175(m)	1169(m)	
1121(m)	1122(m)	1124(m)	1124(m)	1125(m)	1119(m)	
1012(w)	1012(w)	1012(w)	1012(w)	1010(w)	1015(w)	
975(w)	979(w)	979(w)	979(w)	979(w)	978(w)	
936(w)	939(w)	936(w)	935(w)	935(w)	935(w)	
761(s)	760(sh)	760(sh)	760(sh)	760(sh)	760(sh)	δ(C-H) (Ph)
623(m)	620(w)	625(w)	625(w)	625(w)	625(w)	
530(w)	530(w)	532(w)	530(w)	530(w)	530(w)	
---	---	491	---	---	---	ν(M-O)
457(m)	459(m)	459(m)	459(m)	462(m)	460(m)	
---	419(w)	422(w)	423(w)	427(w)	419(w)	ν(M-N)

Abbreviations : s = strong, m = medium, w = weak

L - QSC, I - [Mn(QSC)Cl_2], II - [Fe(QSC)Cl_3], III - [Co(QSC)Cl_2],
IV - [Ni(QSC)Cl_2], V - [Cu(QSC)Cl_2]

carbonyl oxygen atom in this complex. The ligand exhibits a strong band, around 1585 cm^{-1} which might be due to the $\nu(C=N)$ of the quinoxaline ring[9]. This band is shifted to around 1545 cm^{-1}, in the spectra of all the complexes, showing that the ring nitrogen is involved in coordination to the metal atom in all the cases.

4.3.3: *Electronic Spectra*

The electronic spectra of all the complexes were recorded in methanol. The observed bands and their assignments are given in Table IV.4. The strong absorptions observed around 40000 cm^{-1} and 45000 cm^{-1} in the spectra of all the complexes may be due to intraligand transitions. Further, all the complexes exhibit strong bands in the range 32000 cm^{-1} and 28000 cm^{-1} which may be assigned to charge transfer transitions.

The electronic transitions from the $^6A_1$ ground state of manganese(II) to higher energy states are spin-forbidden[10]. These transitions are not observed in the spectrum of the present manganese(II) complex. In high spin iron(III) octahedral complexes, all the d-d transitions are Laporte and spin forbidden and are not observed normally[11,12]. However, a very weak band is observed at 18800 cm^{-1} in the spectrum of the present iron(III) complex. Occurance of such forbidden transitions have been reported in some cases of octhedral iron(III) complexes[13].

Table IV.4

Electronic Spectral Data

Complex	Abs. Max. (cm^{-1})	log ε	Assignments
$[Mn(QSC)Cl_2]$	46800	4.36	Intraligand transitions
	40000	4.09	Intraligand transitions
	32350	3.75	Charge transfer transition
	28940	3.39	Charge transfer transition
$[Fe(QSC)Cl_3]$	32350	3.85	Charge transfer transition
	18800	1.23	d-d transition
$[Co(QSC)Cl_2]$	46600	4.46	Intraligand transitions
	39680	3.67	Intraligand transitions
	28200	3.25	Charge transfer transition
	18650	1.53	$^4A_2 \longrightarrow {}^4T_{1(P)}$
	6960	0.95	$^4A_2 \longrightarrow {}^4T_{1(F)}$
$[Ni(QSC)Cl_2]$	45830	4.40	Intraligand transitions
	40740	4.27	Intraligand transitions
	28170	3.35	Charge transfer transition
	14860	1.77	$^3T_1(F) \longrightarrow {}^3T_1(P)$
	6930	0.94	$^3T_1(F) \longrightarrow {}^3A_2$
$[Cu(QSC)Cl_2]$	49510	4.28	Intraligand transitions
	40700	4.14	Intraligand transitions
	31450	3.35	Charge transfer transition
	28200	3.25	Charge transfer transition
	18870	1.69	$B_{1g} \longrightarrow {}^2E_g$

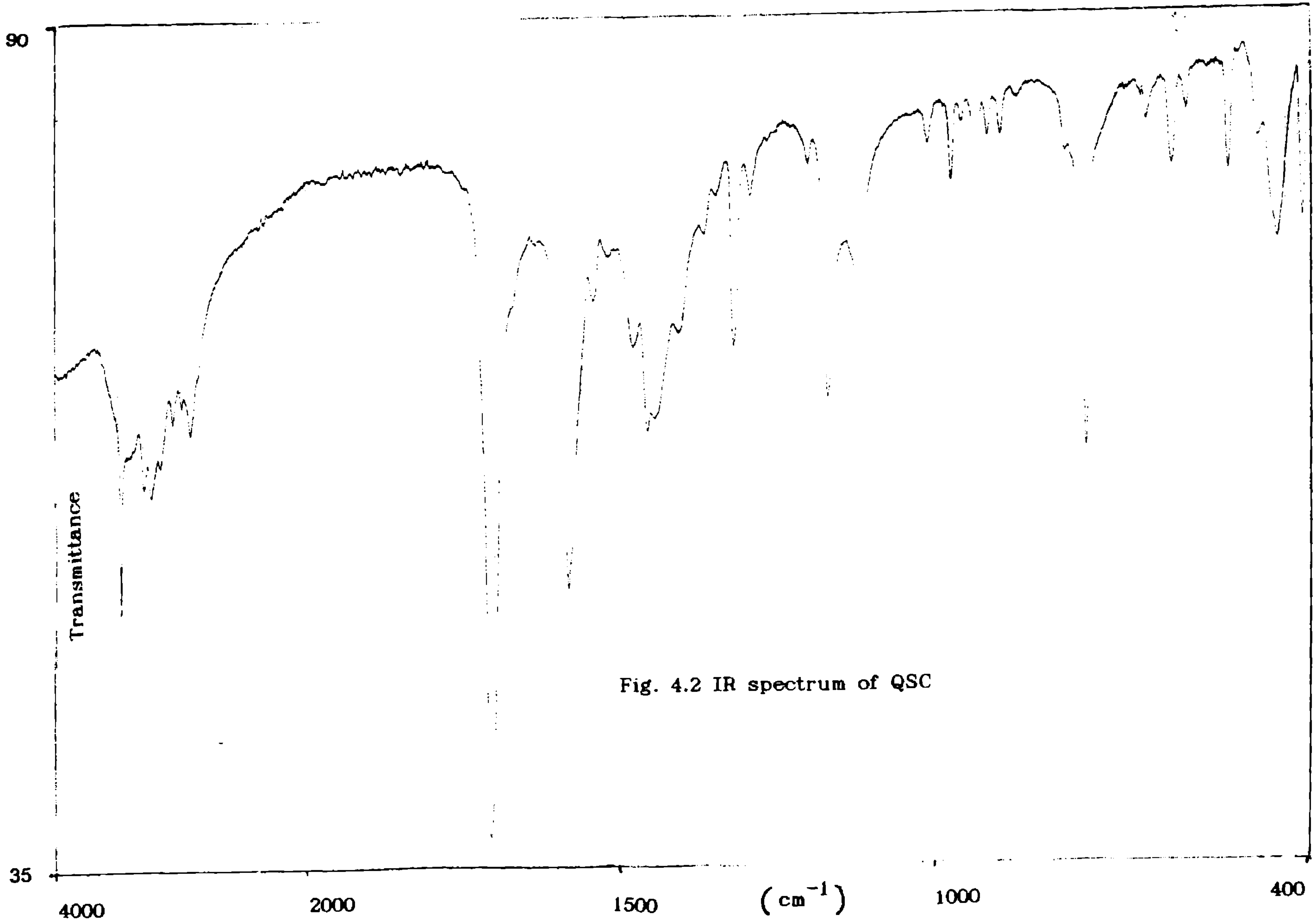


Fig. 4.2 IR spectrum of QSC

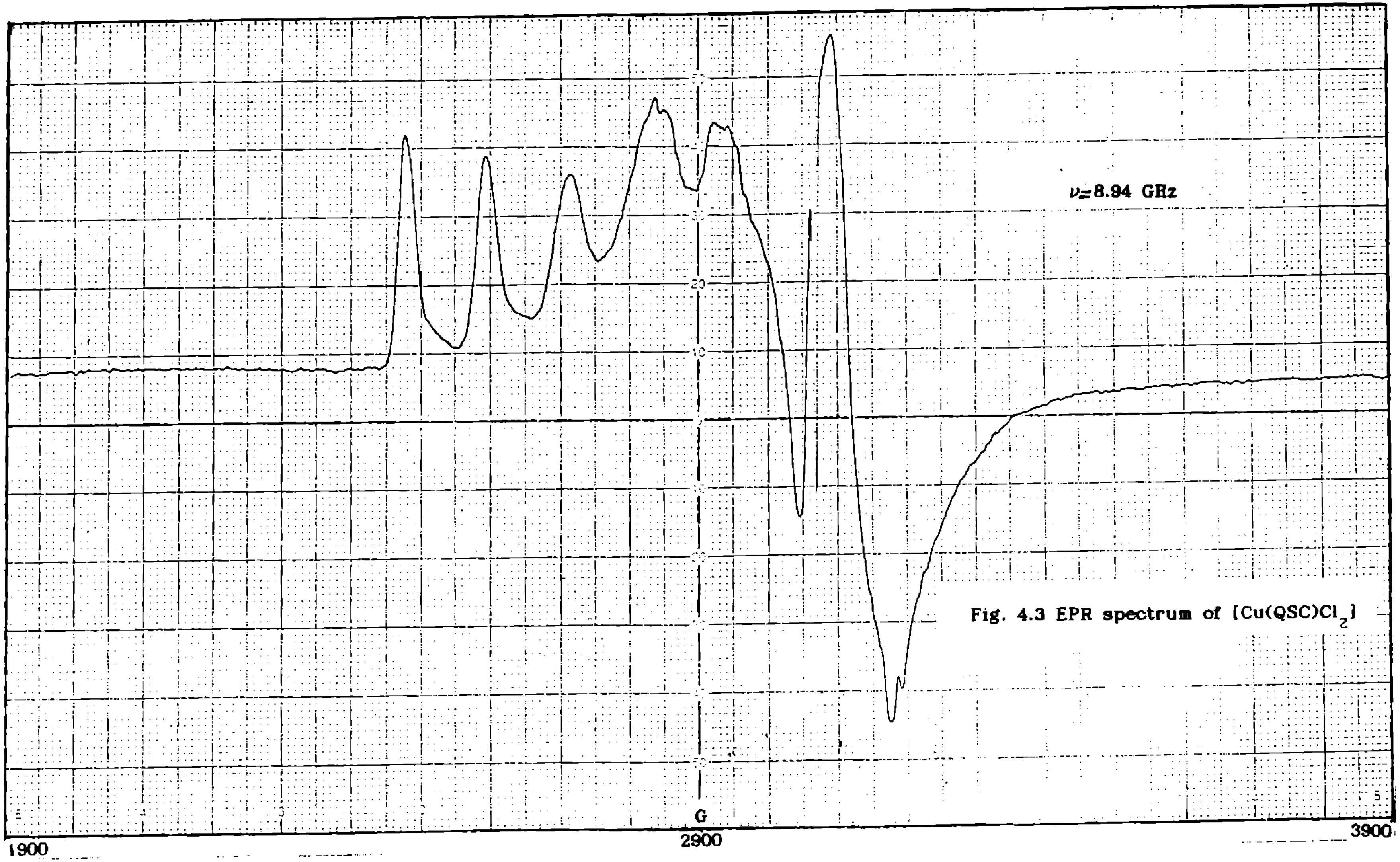


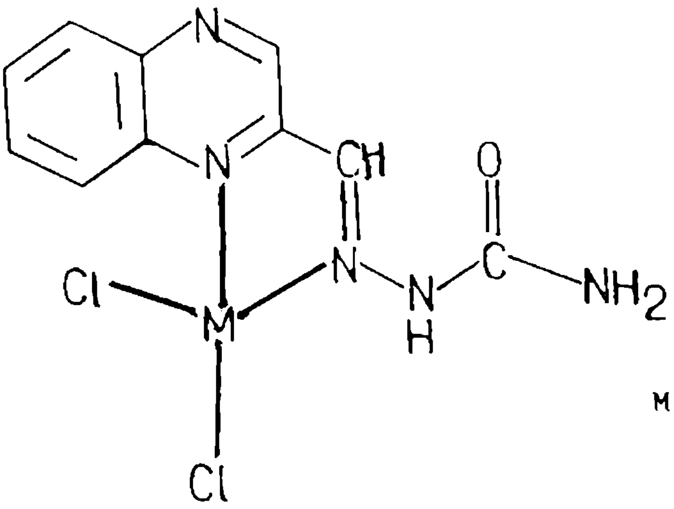
Fig. 4.3 EPR spectrum of $[Cu(QSC)Cl_2]$

The electronic spectrum of cobalt(II) complex shows absorption bands at 18650 cm^{-1} and 6960 cm^{-1} which may be assigned to the transitions $^4A_2 \longrightarrow {}^4T_1(P)$ and $^4A_2 \longrightarrow {}^4T_1(F)$ respectively in a tetrahedral field[14]. In the case of nickel(II) complexes, two transitions are observed at 14860 cm^{-1} and 6930 cm^{-1} which also indicate a tetrahedral geometry around the nickel(II) ion[15]. The electronic spectrum of copper(II) complex exhibits a broad band centered at 18870 cm^{-1}, characteristic of $^1B_{1g} \longrightarrow {}^2E_g$ transition in square-planar environment of the metal ion[16].

4.3.4. *EPR Spectra*

The EPR spectrum (Fig 4.3) of $[Cu(QSC)Cl_2]$ was recorded in DMSO at LNT. The g and A values obtained are $g_1 = 2.4$, $g_2 = 2.2$, $g_3 = 2.06$; $A = 120$ G. These values are in agreement with those of other square planar copper complexes[17].

Based on the above studies the structures shown in Figures 4.4, 4.5 and 4.6 are tentatively proposed for the complexes.



M = Mn(II), Co(II)

or Ni(II)

Fig. 4.4 Schematic structure of the complexes

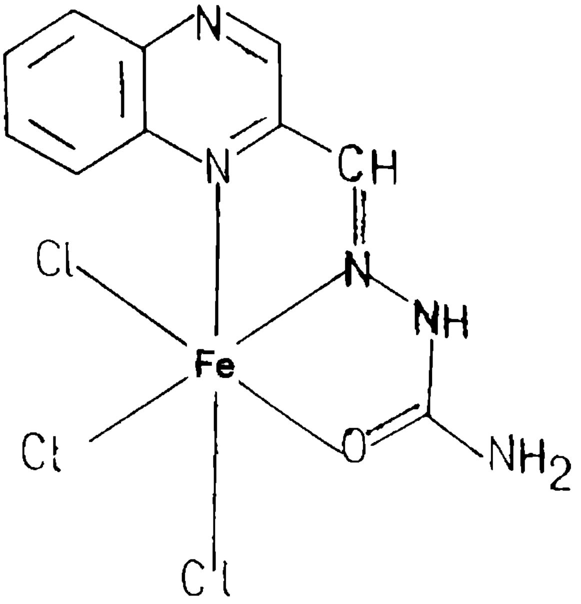


Fig. 4.5 Schematic structure of $[Fe(QSC)Cl_3]$

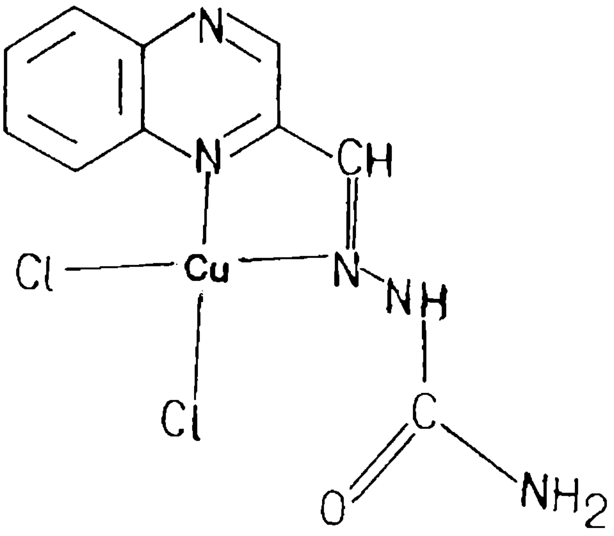


Fig. 4.6 Schematic structure of $[Cu(QSC)Cl_2]$

REFERENCES

1. B. A. Gingras, R. W. Hornal and C. H. Baylay, Canad. J. Chem., 38 (1960) 712.

2. V. K. Arora, K. B. Pandeya and R. P. Singh, J. Indian Chem. Soc., LVI (1979) 6563.

3. P. L. Maurya, B. V. Agarwala and A. K. Dey, J. Indian Chem. Soc., LVII (1980) 275.

4. D. K. West, S. L. Dietrich, I. Thientanavanich and C. A. Brown. Trans. Met. Chem., 19 (1994) 195.

5. F. A. Cotton and E. Bannister, J. Chem. Soc. (1960) 1873.

6. M. Kwiatkowski and G. Bandoli, J. Chem. Soc. Dalton Trans. (1992) 379.

7. C. Preti and G. Tosi, J. Inorg. Nucl. Chem, 38 (1976) 1746.

8. R. C Misra, B. K. Mohapatra and D. Panda, Indian J. Chem., 21A (1982) 188.

9. K. Nakanishi and P. H. Solomon, "Infrared Absorption Spectroscopy", Holden - Day, San Fransisco, 1977.

10. K. S. Siddiqui, M. A. A. Shah and S. A. A. Zaidi, Indian J. Chem., 22A (1983) 812.

11. A. B. P. Lever "Inorganic Electronic Spectroscopy" Elsevier, New York (1968).

12. K. K. M Yusuff and R. Sreekala, Synth. React. Inorg. Met. -Org. Chem., 21 (4), (1991) 553.

13. A. K. Rana and J. R. Saha, Indian J. Chem., 20A (1982) 929.

14. S. N. Dubey and B. Kaushik, Indian J. Chem, 24A (1985) 950.

15. R. S. Drago,"Physical Methods in Inorganic Chemistry", Saunders, Philadelphia (1969).

16. A. Syamal, J. Inorg. Nucl. Chem, 31 (1969) 1869.

17. B. Prabhakar, P. Lingaiah and K. L. Reddy, Polyhedron, 9 (1990) 805.

CHAPTER V

QUINOXALINE-2-CARBOXALIDENE-*O*-PHENYLENEDIAMINE COMPLEXES OF MANGANESE(II), IRON(III), COBALT(II), NICKEL(II) AND COPPER(II)

5.1 INTRODUCTION

Schiff bases obtained by the condensation of diamines with various aldehydes are an interesting class of ligands[1,2]. One of the aims of studies on such complexes was to obtain complexes with higher coordination numbers[3-6], which are rather unusual for transition metals. Schiff bases formed by the condensation of *o*-phenylenediamine with salicylaldehyde or β-diketone have been reported[7]. Compounds of this type are known to form quadridentate chelates with a number of divalent cations[8-10]. The use of these reagents in solvent extraction and determination of copper(II) ions by spectrophotometry or by atomic absorption spectroscopy have also been reported[11]. In this chapter, the synthesis and characterisation of manganese(II), iron(III), cobalt(II), nickel(II) and copper(II) complexes of the Schiff base quinoxaline-2-carboxalidene-*o*-phenylenediamine (QOD) is described.

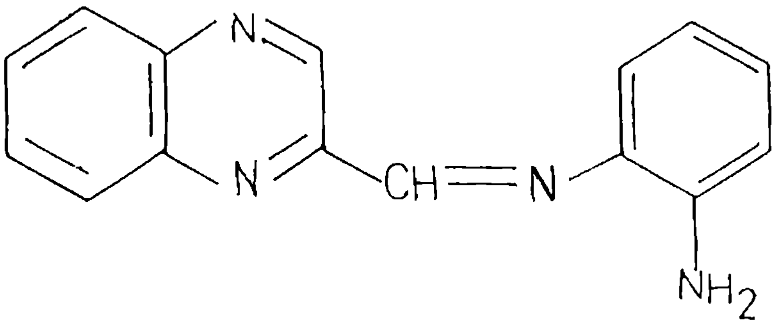


Fig. 5.1 Structure of QOD

5.2 EXPERIMENTAL

5.2.1 *Materials*

The procedure for the preparation of quinoxaline-2-carboxalidene-o-phenylenediamine and details about the reagents are already described in Chapter II.

5.2.2 *Synthesis of the Complexes*

The following general synthetic procedure was used for all the complexes. A solution of the ligand (0.01 mol; 2.48 g) in chloroform (100 mL) was mixed with the corresponding metal salt solution in methanol (0.005 mol; 0.99 g $MnCl_2.4H_2O$, 0.811 g $FeCl_3$, 1.91 g $CoCl_2.6H_2O$, 1.91 g $NiCl_2.6H_2O$ or 0.85 g $CuCl_2.4H_2O$). The solution was refluxed on a waterbath for 10 minutes. The solid complexes separated out were filtered, washed with chloroform and dried *in vacuo* over anhydrous calcium chloride (Yield: 60–70%, M.P.> 250^{o}C).

5.2.3 *Analytical Methods*

The techniques employed for the characterisation of metal complexes are given in Chapter II.

5.3 RESULTS AND DISCUSSION

All the complexes are stable in air and are non-hygroscopic. The complexes are soluble in ethanol, methanol, acetonitrile, DMF and DMSO.

Table V.1

Physical and Analytical Data

Complex	Yield (%)	C % Found (Calc.)	H % Found (Calc.)	N % Found (Calc.)	M % Found (Calc.)	Cl % Found (calc.)
$[Mn(QOD)Cl_2]$	60	47.99 (48.15)	3.07 (3.20)	14.83 (14.90)	14.51 (14.69)	18.91 (18.96)
$[Fe(QOD)Cl_3]$	65	43.79 (43.87)	2.81 (2.90)	13.50 (13.60)	13.13 (13.20)	25.30 (25.90)
$[Co(QOD)Cl_2]$	70	47.44 (47.60)	3.10 (3.17)	14.59 (14.82)	15.30 (15.60)	18.67 (18.80)
$[Ni(QOD)Cl_2]$	70	47.35 (47.70)	3.10 (3.20)	14.40 (14.83)	15.20 (15.50)	18.50 (18.81)
$[Cu(QOD)Cl_2]$	70	46.84 (47.10)	3.07 (3.10)	14.51 (14.60)	16.43 (16.60)	18.37 (16.53)

The molar conductance values (Table V.2) reveal that the complexes are non-electrolytes in methanol.

5.3.1 *Magnetic Susceptibility Measurements*

Magnetic moment values of the complexes are given in Table V.2. The observed μ_{eff} value of manganese(II) complex is 5.7 B.M. which indicates the presence of five unpaired electrons and gives no information about its stereochemistry as already mentioned in chapters III and IV. The magnetic moment of 5.8 B.M. for the iron(III) complex indicates monomeric high-spin iron(III) structures[12-14]. The μ_{eff} values of 4.6 B.M. and 4.1 B.M. for the cobalt(II), and nickel(II) complexes are in agreement with a tetrahedral structure[15,16]. The magnetic moment of 2.0 B.M. for the present copper(II) complex is indicative of a distorted tetrahedral structure[17].

5.3.2 *Infrared Spectra*

The infrared spectral data are given in Table V.3. The strong sharp band at 3376 cm^{-1} may be attributed to ν(N-H) of the amino group. This is found to be shifted to lower regions in all the complexes, showing that the amino group is involved in complexation with the metal ion in all the cases. The spectrum of the free ligand shows an intense band at 1608 cm^{-1}, which may be assigned to ν(C=N) of the azomethine group. This band undergoes a red shift in all the complexes, indicating the participation of azomethine nitrogen atom in coordination[18]. The band observed at 1580 cm^{-1} in the spectrum of the ligand may be assigned

Table V.2

Molar Conductance and Magnetic Moment Data

Complex	Colour	Magnetic Moment (B.M)	Molar Conductance ($ohm^{-1}cm^{2}mol^{-1}$)
$[Mn(QOD)Cl_2]$	dark yellow	5.7	4.8
$[Fe(QOD)Cl_3]$	light brown	5.8	49.3
$[Co(QOD)Cl_2]$	brick red	4.6	31.7
$[Ni(QOD)Cl_2]$	dark green	4.1	10.8
$[Cu(QOD)Cl_2]$	light brown	2.0	18.7

Table-V.3

Infrared Spectral Data

L	I	II	III	IV	V	Assignments
3376(s)	3350(s)	3346(s)	3346(s)	3333(s)	3333(s)	ν(N-H)
2922(w)	2922(w)	2924(w)	2920(w)	2924(w)	2921(w)	
1608(s)	1589(m)	1591(m)	1590(m)	1592(m)	1592(m)	ν(C=N) azomethine
1580(w)	1580(w)	1564(w)	1585(w)	1580(w)	1582(w)	ν(C=N) ring
1496(s)	1500(s)	1495(s)	1492(s)	1494(s)	1502(s)	
1440(w)	1440(w)	1445(w)	1436(w)	1436(w)	1436(w)	
1366(w)	1366(m)	1367(m)	1369(m)	1364(m)	1365(m)	
1322(m)	1321(m)	1323(m)	1322(m)	1325(w)	1321(m)	
1269(w)	1272(w)	1278(w)	1274(w)	1273(w)	1275(w)	
1208(w)	1214(m)	1214(w)	1211(w)	1209(m)	1211(m)	
1128(m)	1128(w)	1129(m)	1126(m)	1131(s)	1126(s)	
1015(w)	1021(m)	1018(w)	1021	1020(s)	1021(s)	
966(w)	960(w)	956(w)	960(m)	966(w)	960(m)	
898(w)	899(w)	900(w)	900(w)	900(w)	900(w)	
867(w)	867(w)	867(w)	862(w)	866(w)	866(w)	ρ(CH)
759(s)	758(s)	760(s)	759(s)	760(s)	762(s)	ρ(CH)(Ph)
——	496(w)	502(w)	502(w)	500(w)	499(w)	ν(M-N)
463(w)	465(sh)	467(w)	467(w)	466(w)	466(w)	
409(m)	412(m)	411(m)	410(m)	412(m)	412(m)	

Abbreviations:- s = strong, m = medium, w = weak and sh = shoulder

L - QOD, I - [Mn(QOD)Cl_2], II - [Fe(QOD)Cl_3],
III - [Co(QOD)Cl_2], IV - [Ni(QOD)Cl_2] and V - [Cu(QOD)Cl_2]

to ν(C=N) of the quinoxaline ring. This band is shifted to lower regions in the spectrum of the iron(III) complex, whereas in all other cases it is found to be retained at 1580 cm^{-1}. This shows that the nitrogen atom of the quinoxaline ring is not coordinated to the metal in any of the complexes except in the iron(III) complex. In all the complexes an additional band appears near 500 cm^{-1} which can be assigned to ν(M-N) in these complexes[19]. From these observations it is seen that the ligand QOD is acting as a bidentate ligand coordinating through the amino group and the azomethine group in manganese(II), cobalt(II), nickel(II) and copper(II) complexes. In the iron(III) complex the ring nitrogen of the quinoxaline ring is also taking part in complexation.

5.3.3 *Electronic Spectra*

The electronic spectra of all the complexes were recorded in methanol and the data obtained are shown in Table V.4.

The strong absorptions observed around 40000 cm^{-1} in the spectra of all the complexes may be due to the intraligand transitions. Further all the complexes exhibit strong bands in the range 33000 cm^{-1} and 27000 cm^{-1} which can be assigned to charge-transfer transitions.

In the electronic spectrum of manganese(II) complex there is a very weak band at 22900 cm^{-1} which can be assigned to d-d transition, which is frequently observed as a weak band in tetrahedral environment[20]. In the spectrum of iron(III) complex no d-d bands are observed. This may be due to the strong charge-transfer bands masking the low intensity

Table V.4

Electronic Spectral Data

Complex	Abs. Max. (cm^{-1})	log ε	Assignments
$[Mn(QOD)Cl_2]$	40350	4.4	Intraligand transitions
	28750	3.75	charge transfer transitions
	22900	1.1	d-d transition
$[Fe(QOD)Cl_3]$	40000	4.4	Intraligand
	30910	3.64	charge transfer transitions
	22030	3.23	charge transfer transitions
$[Co(QOD)Cl_2]$	40940	4.45	Intraligand transitions
	32800	3.78	charge transfer transitions
	28800	3.65	charge transfer transitions
	18800	1.34	$^4A_2 \longrightarrow {}^4T_1(P)$
	6890	0.94	$^4A_2 \longrightarrow {}^4T_1(F)$
$[Ni(QOD)Cl_2]$	41620	4.35	Intraligand transitions
	33000	3.87	charge transfer transitions
	23920	3.4	charge transfer transitions
	17630	1.37	$^3T_1(F) \longrightarrow {}^3T_1(P)$
	6890	0.84	$^3T_1(F) \longrightarrow {}^3A_2$
$[Cu(QOD)Cl_2]$	40350	4.39	Intraligand transitions
	29300	3.95	charge transfer transitions
	27000	3.25	charge transfer transitions
	21420	1.11	d-d transition

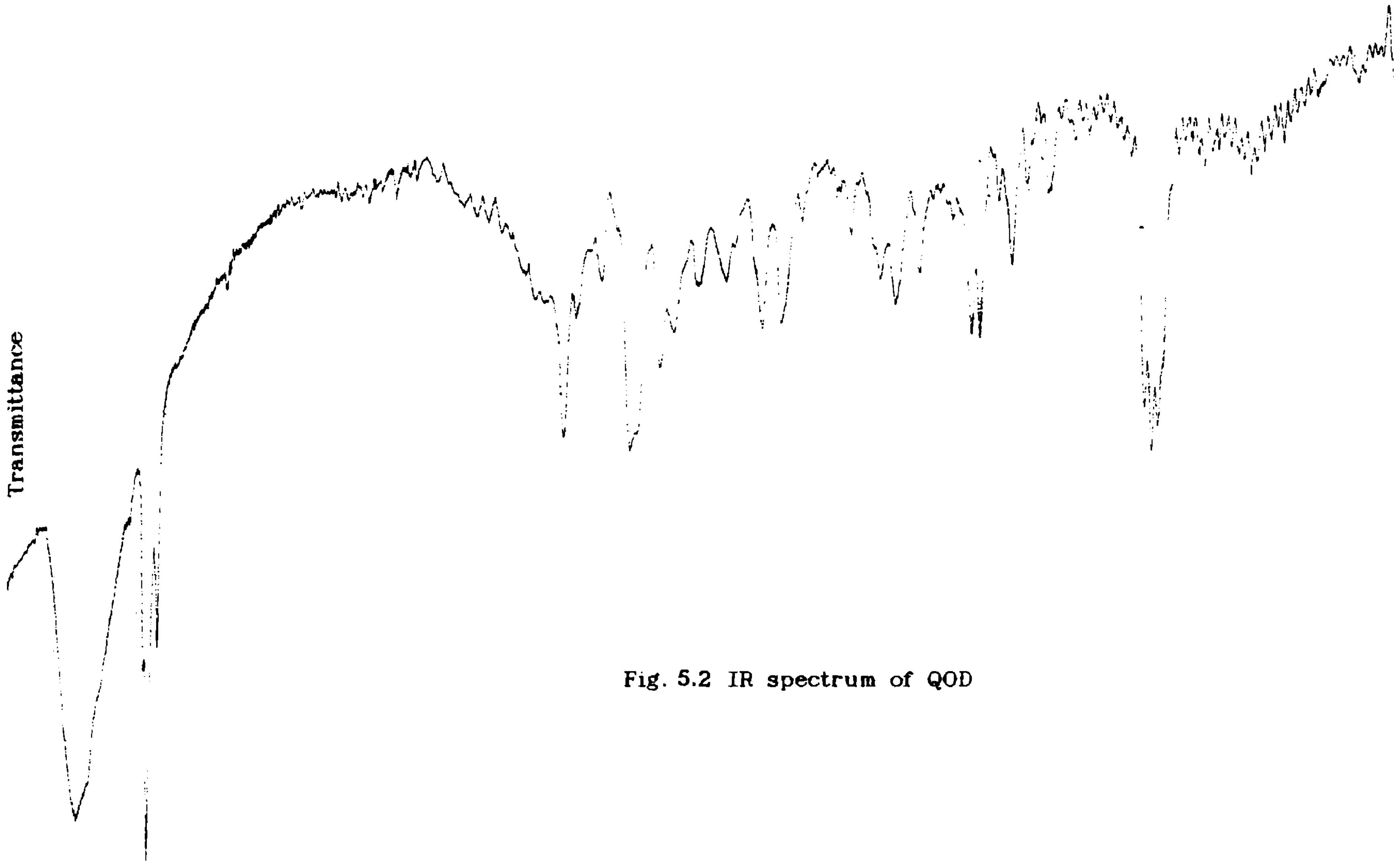


Fig. 5.2 IR spectrum of QOD

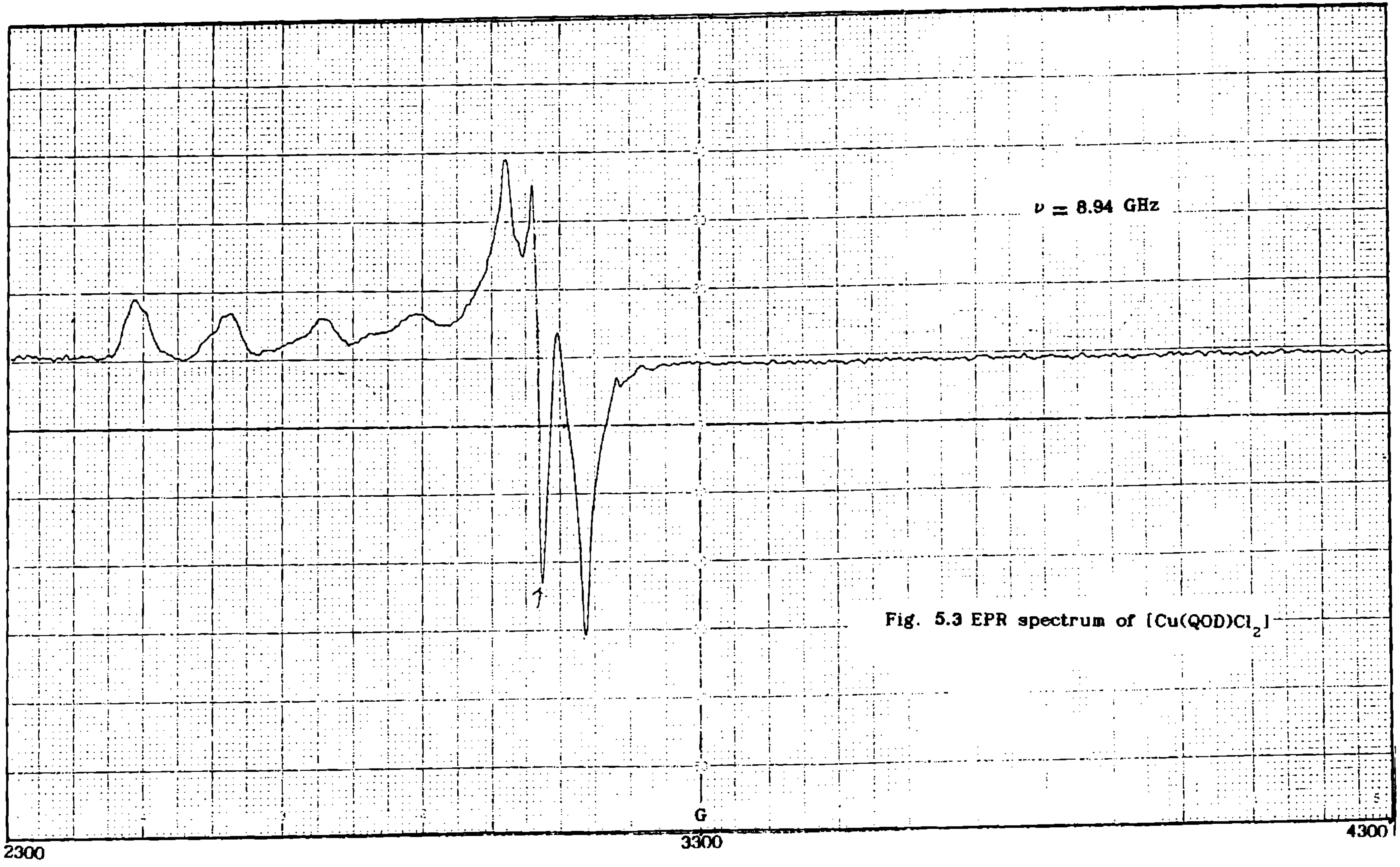


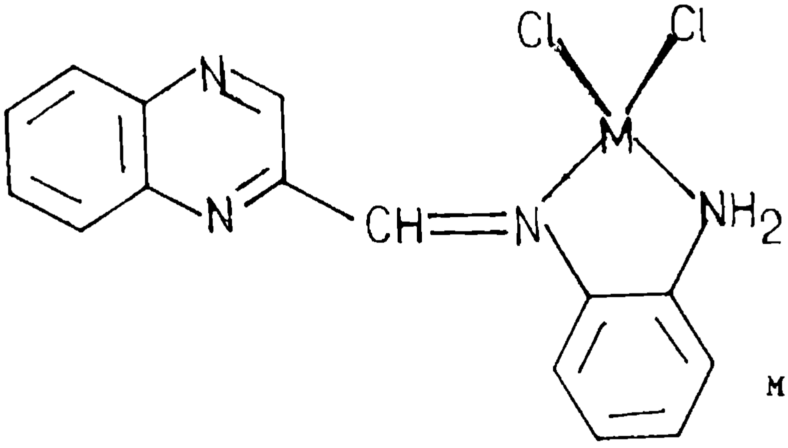
Fig. 5.3 EPR spectrum of [Cu(QOD)Cl_2]

forbidden d-d bands[21,22]. The cobalt(II) complex exhibits a band at 18800 cm^{-1}, which may be assigned to the $^4A_2(F) \longrightarrow {}^4T_1(P)$ transition[23]. The band observed in the near IR region at 6890 cm^{-1}, may be attributed to $^4A_2 \longrightarrow {}^4T_1(F)$ transition[24]. The nickel(II) complex shows a band at 17630 cm^{-1}, which can be assigned to the $^3T_1(F) \longrightarrow {}^3T_1(P)$ transition, which is observed in tetrahedral geometry[25]. The near IR band characteristic of the $^3T_1(F) \longrightarrow {}^3A_2(F)$ transition of tetrahedral nickel(II) appears at 6890 cm^{-1} for this complex. Copper(II) complex shows a broad d-d band in the region 21420 cm^{-1} which is in agreement with other reported cases of tetrahedral copper(II) complexes[26].

5.3.4 *EPR Spectral Data*

The EPR spectrum (Fig. 5.3) of [Cu(QOD)Cl$_2$] was recorded in DMSO at LNT. The g and A values are g_1 = 2.17, g_2 = 1.9, g_3 = 1.8 and A = 135 G. By comparing with similar spectra, it can be seen that the values are in agreement with a structure which is intermediate between tetrahedral and planar structures[27].

Based on the above findings, the structures shown in Figures 5.4 and 5.5 are proposed for the complexes.



M = Mn(II), Co(II)
Ni(II) and Cu(II)

Fig. 5.4 Schematic structure of [M(QOD)Cl$_2$]

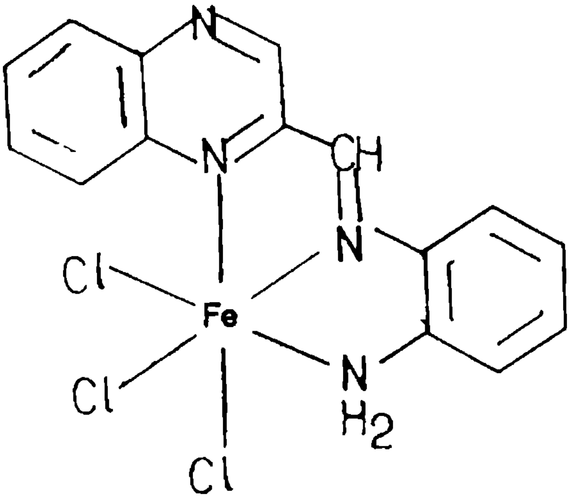


Fig. 5.5 Schematic structure of [Fe(QOD)Cl$_3$]

REFERENCES

1. H. Masaaki, and K. Kyoko, Inorg. Chim. Acta, 104 (1985) 47.

2. S. Singh, V. Chakravortty and K. C. Dash, Indian J. Chem., 29A (1990) 713.

3. H. N. Mohanta and K. C. Dash, J. Inorg Nucl Chem., 39 (1977) 1345; J. Indian Chem. Soc., 57 (1980) 26.

4. H. N .Mohanta and K. C. Dash, Indian J. Chem., 15A (1977) 657; Synth. React. Inorg. Met. -Org. Chem., 8 (1978) 43; 9 (1979) 325; Russ. J. Inorg. Chem., 25 (1980) 586.

5. C. R. Panda, V. Chakravortty and K. C. Dash, J. Less-common Metals, 135 (1987) 77.

6. S. Singh, V. Chakravortty and K. C. Dash, Indian J. Chem., 28A (1989) 255.

7. J. Agget and R. A. Richardson, Anal. Chem. Acta, 50 (1970) 269.

8. D. Hall, H. J. Morgan and T. N. Waters, J. Chem. Soc., A (1966) 677.

9. G. R. Clark, D. Hall and T. N. Waters, J. Chem. Soc., A (1968) 223.

10. E. N. Baker, D. Hall, A. J. McKinnon, T. N. Waters, Chem. Commun., (1967) 134.

11. J. Agget, A. W. Khoo and R. A. Richardson, J. Inorg. Nucl. Chem., 43 (1981) 1867.

12. R. L. Lintvedt and L. A. Kernitsky, Inorg. Chem., 9 (1970) 491.

13. V. M. Leovic, L. J. Bielica, L. S. Jovanovic and S. Y. Chung, Polyhedron, 5 (1986) 983.

14. N. N. Greenwood and A. Earnshaw, "Chemistry of the elements", Pergamon Press, Oxford, (1989) 1346.

15. C. R. Chaudhury and K. C. Dash, Indian J. Chem. 17A (1979) 364.

16. P. Bamfield, J. Chem. Soc. A, (1967) 804.

17. R. S. Sager and W. H. Watson, Inorg. Chem., 6 (1967) 946.

18. R. S. Drago, "Physical Methods in Inorganic Chemistry", Saunders, Philadelphia (1969).

19. S. G. Valavi and K. K. M. Yusuff, Synth. React. Inorg. Met.-Org. Chem., 25 (1996) 1309.

20. K. Dey, A. K. Biswas and A. K. S. Roy, Indian J. Chem., 20A (1981) 848.

21. J. T. Donoghue and R. S. Drago, Inorg. Chem., 1 (1962) 866.

22. J. A. Bertrand and D. G. Eller, Inorg. Chem., 13 (1974) 927.

23. K. S. Murray, Coord. Chem. Rev., 12 (1974) 1.

24. S. N. Dubey and B. Kaushik, Indian. J. Chem., 24A (1985) 950.

25. R. H. Holm, A. Chakraworthy and L. J. Theriot, Inorg. Chem., 5 (1966) 625.

26. H. K. Sharma, S. Lata, S. N. Dubey and D. M. Puri., Indian. J. Chem., 20A (1981) 1031.

27. R. C. Rosenberg, C. A. Root, P. K. Bernstein and H. B. Gray, J. Am. Chem. Soc., 97 (1975) 2092.

CHAPTER VI

QUINOXALINE-2-CARBOXALIDENE-2-FURFURYLAMINE COMPLEXES OF MANGANESE(II), IRON(III), COBALT(II), NICKEL(II) AND COPPER(II)

6.1 INTRODUCTION

Heteroaromatic Schiff base complexes have great biological significance. Many such complexes are reported to have antibacterial, antifungal, tuberculostatic and anticancerous properties[1,2]. Literature survey revealed that there are only a few reports on the studies of Schiff base complexes derived from the heterocyclic aldehyde, quinoxaline-2-carboxaldehyde. Hence it was thought to be worthwhile to synthesise a new heterocyclic Schiff base derived from this aldehyde and a heterocyclic amine namely furfurylamine and its complexes. In this chapter, we present our studies on manganese(II), iron(III), cobalt(II), nickel(II) and copper(II) complexes of the Schiff base quinoxaline-2-carboxalidene-2-furfurylamine (QFA).

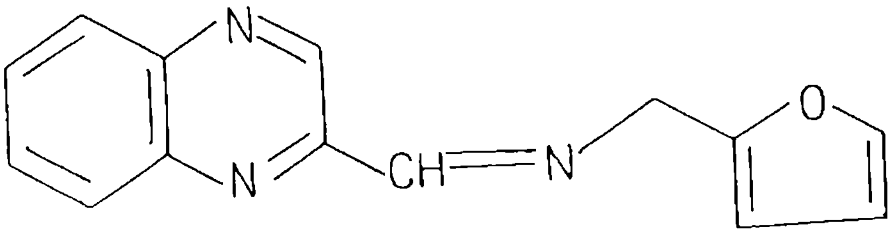


Fig. 6.1 Structure of QFA

6.2 EXPERIMENTAL

6.2.1 *Materials*

Details regarding the reagents and preparation of the ligand are given in Chapter II.

6.2.2 *Synthesis of the Complexes*

All the complexes were prepared by the following general procedure:

Quinoxaline-2-carboxaldehyde (0.01 mol; 1.58 g) was dissolved in dichloromethane (50 mL). Furfurylamine (0.01 mol; 0.88 mL) was then added directly to the solution and the mixture was then refluxed for about 15 minutes. The solution of the corresponding metal salt (0.01 mol; 0.985 g $MnCl_2.4H_2O$, 0.811 g $FeCl_3$, 1.190 g $CoCl_2.6H_2O$, 1.190 g $NiCl_2.6H_2O$ or 0.85 g $CuCl_2.2H_2O$) in methanol (50 mL) was then added to the above solution and the resultant solution was refluxed for about 30 minutes. The solution was concentrated by evaporation and cooled in a freezer. The complexes separated out were filtered, washed with ether and dried *in vacuo* over anhydrous calcium chloride (Yield 50–60%, M.P:> 250°C).

6.2.3 *Analytical Methods*

Details regarding the analytical methods and other characterisation techniques employed are already described in Chapter II.

6.3 RESULTS AND DISCUSSION

All the complexes are stable in air and are non-hygroscopic. Analytical data (Table VI.1) show that manganese(II), cobalt(II) and nickel(II) complexes have the general empirical formula, $[M(QFA)_2Cl_2]$. The formulae of iron(III) and copper(II) complexes are $[Fe(QFA)(OH)_2Cl]$ and $[Cu(QFA)Cl_2]$ respectively. The complexes are soluble in ethanol, methanol, acetonitrile, DMF and DMSO. The molar conductance values show that they are non-electrolytes in nitrobenzene.

6.3.1 *Magnetic Susceptibility Measurements*

Magnetic moment values are given in Table VI.2. The manganese(II) complex exhibits a magnetic moment of 5.8 B.M., which corresponds to the presence of five unpaired electrons. Iron(III) complex has a μ_{eff} value of 5.2 B.M., which is less than that expected for spin free Fe(III) complexes. This lowering may be due to the antiferromagnetic coupling, resulting from a dimeric structure[3-12]. The room temperature magnetic moments of cobalt(II) and nickel(II) complexes are 5.1 B.M. and 3.0 B.M. respectively, which suggest an octahedral stereochemistry around the metal ion[13,14]. Copper(II) complex exhibits a magnetic moment of 2.2 B.M., which indicates a distorted tetrahedral stereochemistry[15] for this complex.

6.3.2 *Infrared Spectra*

The infrared spectral data are given in Table VI.3. The ligand

Table VI.I

Physical and Analytical Data

Complex	Yield (%)	C % Found (Calc)	H % Found (Calc)	N % Found (Calc)	M % Found (Calc)	Cl Found (Calc)
$[Mn(QFA)_2Cl_2]$	55	55.88	3.61	13.95	8.97	11.64
		(56.01)	(3.66)	(14.0)	(9.16)	(11.80)
$[Fe(QFA)(OH)_2Cl]$	50	46.20	3.50	11.44	15.20	9.63
		(46.37)	(3.59)	(11.59)	(15.4)	(9.78)
$[Co(QFA)_2Cl_2]$	60	55.55	3.62	13.60	9.69	11.70
		(55.60)	(3.64)	(13.90)	(9.72)	(11.75)
$[Ni(QFA)_2Cl_2]$	55	55.43	3.61	12.79	9.64	11.65
		(55.70)	(3.64)	(13.00)	(9.72)	(11.75)
$[Cu(QFA)Cl_2]$	60	54.97	3.55	13.63	10.41	11.54
		(55.20)	(3.62)	(13.80)	(10.44)	(11.65)

Table VI.2

Magnetic and Conductance Data

Complex	Colour	Magnetic Moment (B.M.)	Molar Conductance (ohm^{-1} cm^2 mol^{-1})
$[Mn(QFA)_2Cl_2]$	brown	5.8	1.0
$[Fe(QFA)(OH)_2Cl]$	black	5.2	6.0
$[Co(QFA)_2Cl_2]$	brown	5.1	1.0
$[Ni(QFA)_2Cl_2]$	black	3.0	2.4
$[Cu(QFA)Cl_2]$	brown	2.2	4.8

Table VI.3
Infrared Spectral Data

L	I	II	III	IV	V	Assignments
——	——	3450(s)	——	——	——	ν(O-H)
1675(s)	1645(s)	1640(s)	1645(s)	1640(s)	1640(s)	ν(C=N) azomethine
1579(w)	1560(w)	1560(w)	1560(w)	1555(w)	1560(w)	ν(C=N) ring
1540(m)	1538(w)	1540(m)	1540(m)	1540(w)	1540(w)	
1490(s)	1490(s)	1490(s)	1490(s)	1490(s)	1495(s)	
1460(m)	1460(w)	1460(m)	1460(m)	1460(m)	1460(s)	
1380(sh)	1380(m)	1380(s)	1380(s)	1380(s)	1380(w)	
1330(m)	1340(sh)	1335(m)	1340(sh)	1340(w)	1335(w)	
1250(w)	1250(w)	1245(w)	1255(w)	1250(w)	1250(w)	
1210(w)	1210(w)	1210(m)	1210(m)	1210(w)	1210(w)	
1180(w)	1180(w)	1180(w)	1180(w)	1180(w)	1185(w)	
1122(w)	1122(m)	1122(m)	1122(m)	1122(m)	1122(m)	
1073(m)	1070(m)	1070(w)	1073(m)	1073(m)	1069(m)	
1010(s)	1010(s)	1010(s)	1010(s)	1010(s)	1010(s)	
980(w)	980(w)	980(w)	985(w)	985(w)	985(m)	
960(w)	960(w)	960(w)	960(w)	960(w)	960(w)	
882(m)	880(w)	880(w)	880(w)	880(w)	880(w)	
867(w)	867(w)	867(w)	862(w)	866(w)	866(w)	
760(s)	760(s)	760(s)	760(s)	760(s)	755(s)	
——	600(m)	600(s)	600(s)	600(s)	595(m)	ν(M-N)
510(w)	510(w)	515(w)	515(w)	515(w)	515(w)	
490(w)	490(sh)	490(sh)	490(w)	490(w)	495(w)	
455(sh)	455(s)	460(s)	460(w)	460(s)	455(w)	
——	——	410(s)	——	——	——	ν(M-O)

Abbreviations:- s = strong, m = medium, w = weak and sh = shoulder

L - QFA, I - [Mn(QFA)$_2$Cl$_2$], II - [Fe(QFA)(OH)$_2$Cl],

III - [Co(QFA)$_2$Cl$_2$], IV - [Ni(QFA)$_2$Cl$_2$], V - [Cu(QFA)Cl$_2$]

exhibits a strong band at 1675 cm^{-1} which can be assigned to $\nu(C=N)$ of the azomethine group. This band is found to be shifted to ~ 1640 cm^{-1} in all the complexes, indicating the coordination of the azomethine group of the ligand[16]. The $\nu(C=N)$ of the quinoxaline ring which appears at 1579 cm^{-1} in the spectrum of the ligand undergoes a red shift to around 1560 cm^{-1} in the spectra of all the complexes[17]. In the case of the iron(III) complex a strong band appears at 3450 cm^{-1}, which is absent in the spectrum of the ligand. It can be assigned to $\nu(O-H)$ of the hydroxyl group in the complex. Further, a strong band observed at 410 cm^{-1}, in the spectrum of the iron(III) complex may be assigned to $\nu(M-O)$[18], which evidences the coordination of the hydroxyl group to the metal atom. No band is seen at 840 cm^{-1} suggesting the absence of any coordinated water molecules in this complex. These results suggest that the ligand QFA acts as a bidentate ligand in all the complexes coordinating through azomethine nitrogen atom and quinoxaline ring nitrogen atom.

6.3.3 *Electronic Spectra*

The electronic spectral data are given in Table VI.4. In the electronic spectra of all the complexes, intense bands are observed around 40000 cm^{-1} due to intraligand transitions. In addition, all the complexes exhibit charge transfer transitions in the region between 27000–33300 cm^{-1} respectively.

Table VI.4

Electronic Spectral Data of the Complexes

complex	Abs. Max. (cm^{-1})	log ε	Assignments
$[Mn(QFA)_2Cl_2]$	46000	4.36	Intraligand transitions
	37000	4.29	Intraligand transitions
	33300	3.37	charge transfer transitions
	21670	0.89	$^6A_{1g} \longrightarrow {}^4T_{2g}(G)$
$[Fe(QFA)(OH)_2Cl]$	48500	4.48	Intraligand transitions
	41670	4.25	Intraligand transitions
	31150	3.23	charge transfer transitions
$[Co(QFA)_2Cl_2]$	47600	4.45	Intraligand transitions
	42000	4.31	Intraligand transitions
	32350	3.65	charge transfer transitions
	27170	3.34	charge transfer transitions
	22000	1.81	$^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$
$[Ni(QFA)_2Cl_2]$	46730	4.35	Intraligand transitions
	42370	4.22	Intraligand transitions
	30660	3.40	charge transfer transitions
	17600	1.37	$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$
$[Cu(QFA)Cl_2]$	40000	4.43	Intraligand transitions
	28000	3.53	charge transfer transitions
	27000	3.25	charge transfer transitions
	11800	0.99	d-d transition

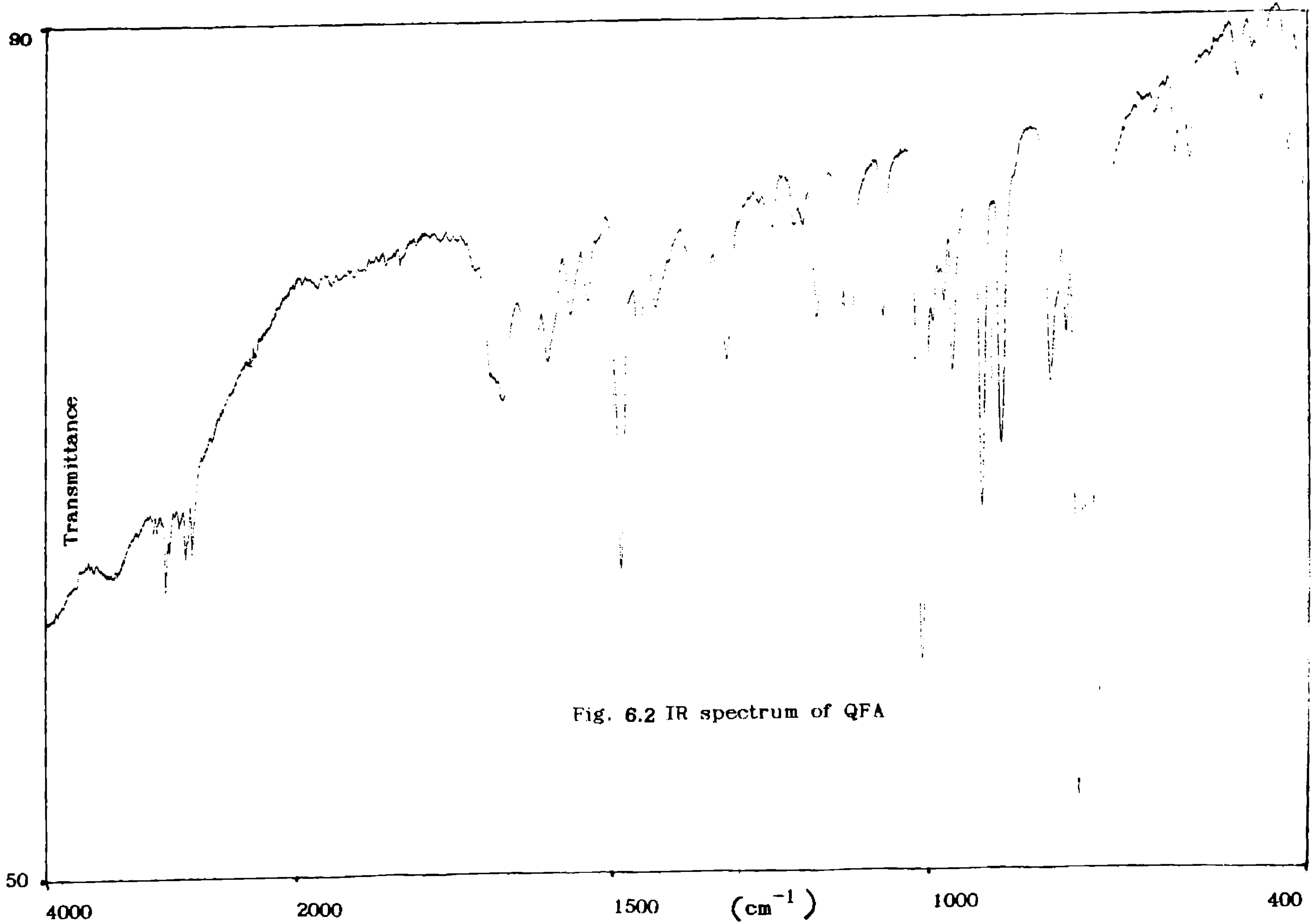


Fig. 6.2 IR spectrum of QFA

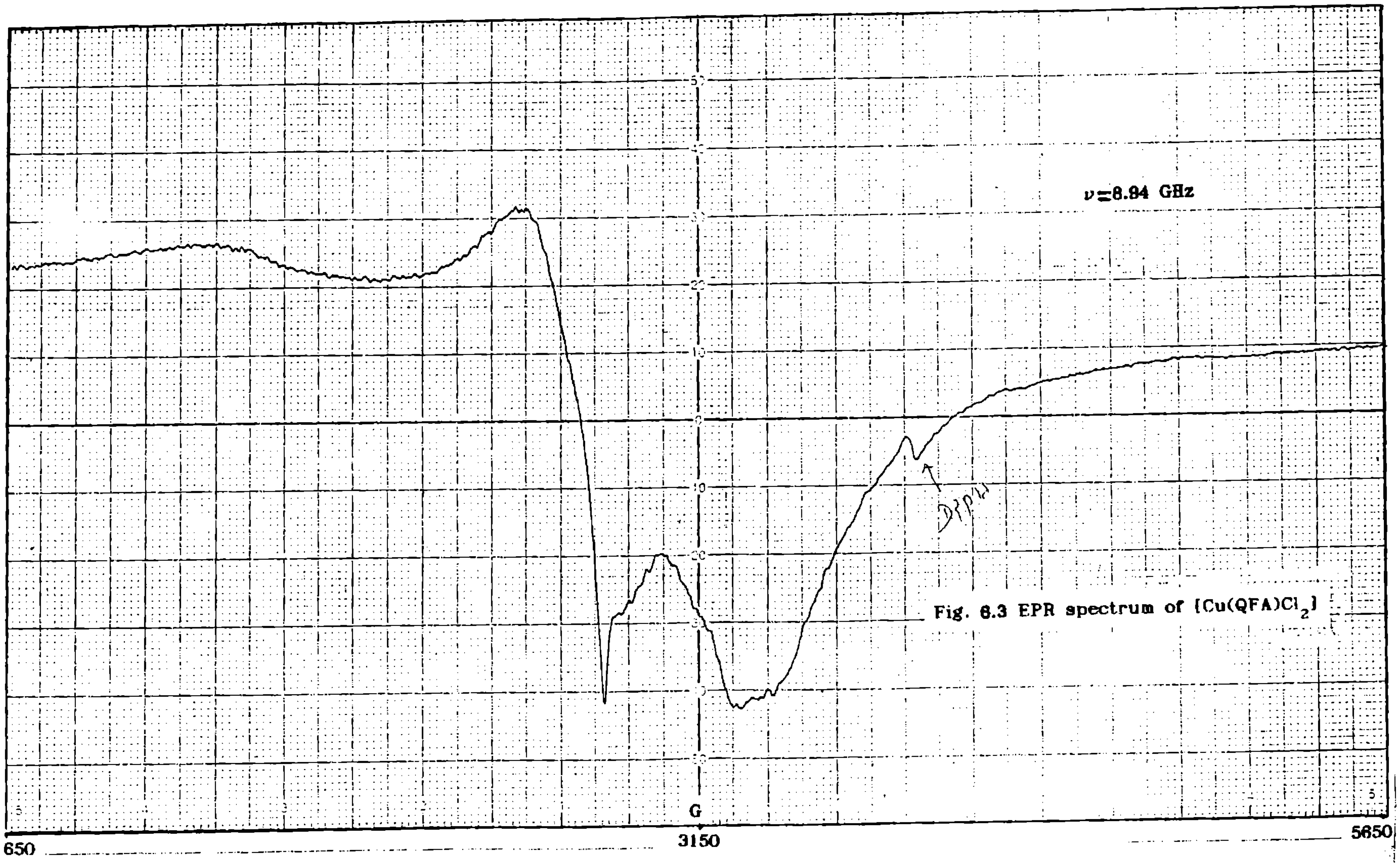


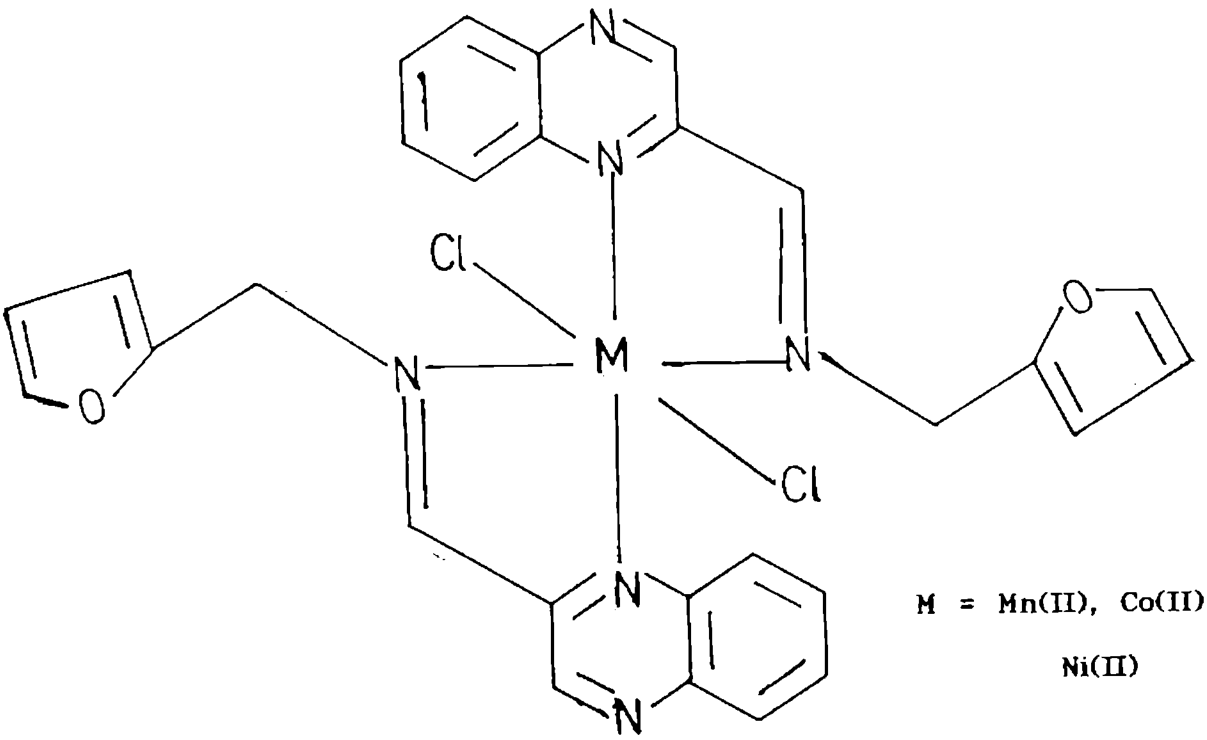
Fig. 6.3 EPR spectrum of [Cu(QFA)Cl$_2$]

The electronic spectrum of the manganese(II) complex shows a weak band around 21670 cm^{-1} and by assuming an octahedral structure, which can be assigned to $^6A_{1g} \longrightarrow {}^4T_{2g}(G)$ transition[19]. For the iron(III) complex no bands are observed in the visible region[20]. In the electronic spectrum of cobalt(II) complex the d-d transitions are almost masked by the high intensity charge transfer bands[21]. However, a shoulder is observed around 22000 cm^{-1} which can be assigned to the $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ transition, and transitions in this region have been reported for octahedral cobalt(II) complexes[22]. The spectrum of the nickel(II) complex exhibits a band at 17600 cm^{-1}, which may be assigned to the transition $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ in an octahedral field around nickel(II)[23, 24]. A broad d-d band is observed at 11800 cm^{-1} for the copper(II) complex[25], which has been reported for copper(II) complexes with distorted tetrahedral structures[25].

6.3.4. *EPR Spectra*

The EPR spectrum (Fig. 6.4) of the copper(II) complex was taken in methanol at liquid nitrogen temperature. The g and A values obtained are, g_1 = 2.07, g_2 = 1.89, g_3 = 1.86 and A value = 115 G, which agrees with the reported results of many distorted tetrahedral copper(II) complexes.

Based on the above investigations, the structures given in Figures 6.4, 6.5 and 6.6 are proposed for the complexes.



M = Mn(II), Co(II) and Ni(II)

Fig. 6.4 Schematic structure of the complexes

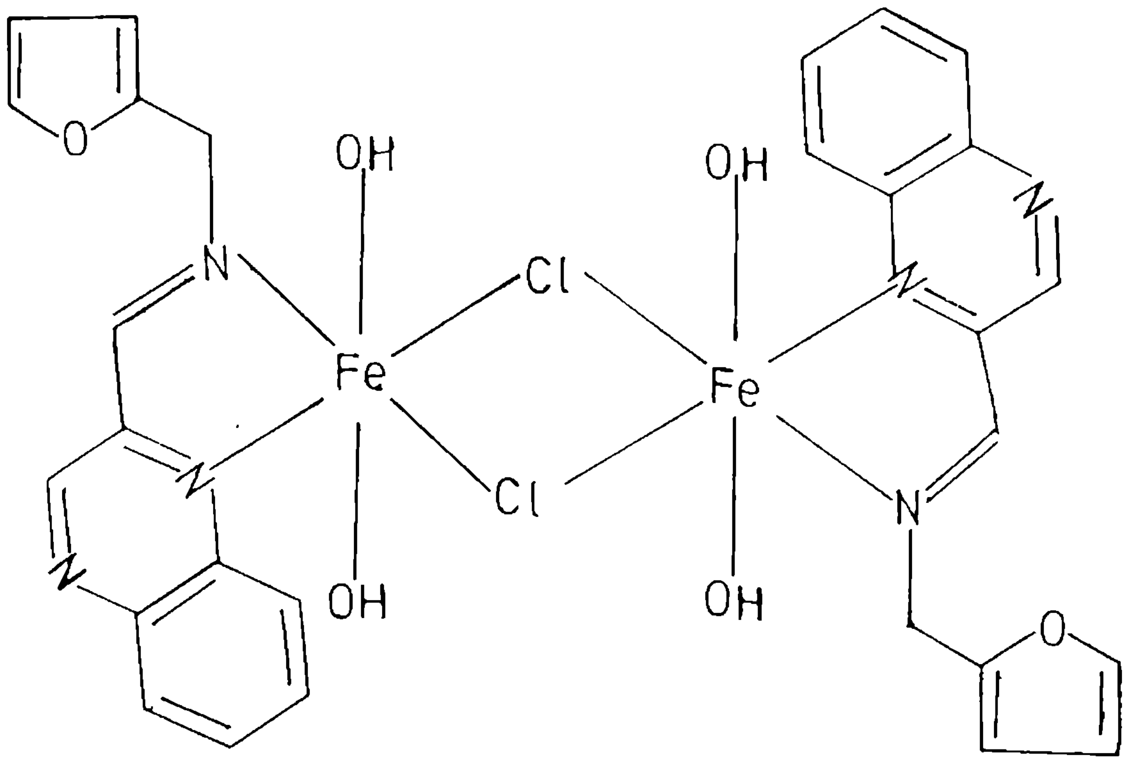


Fig. 6.5 Schematic structure of $[Fe(QFA)(OH)_2Cl]_2$

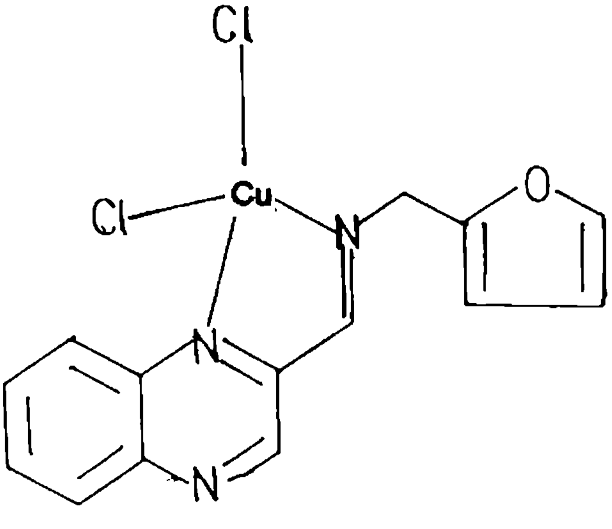


Fig. 6.6 Schematic structure of $[Cu(QFA)Cl_2]$

REFERENCES

1. A. K. Varshney, P. S. Verma and S., Varshney, Synth. React. Inorg. Met-Org. Chem., 19 (1985) 75.

2. P. Chattergee, B. V. Agarwala, A. K. Dey, Synth. React. Inorg. Met.-Org. Chem., 19 (1989) 715.

3. W. Klemm and K. H. Raddatz, Z. Anorg. Chem., 250 (1942).

4. M. Gerloch, J. Lewis, F. E. Mabbs and A. Richards, J. Chem Soc., A, (1968) 112.

5. W. M. Reiff, W. A. Baker, Jr. and N. E. Erickson, J. Am. Chem. Soc., 90 (1968) 6347.

6. R. De. Isasi, S. L. Holt and B. Post, Inorg. Chem., 10 (1971) 1598.

7. W. M. Reiff, G. J. Long and W. A. Baker, Jr., J. Am. Chem. Soc., 90 (1968) 6347.

8. Y. Nishida, K. Kino and S. Kida, J. Chem. Soc. Dalton. Trans., (1987) 1157.

9. R. N. Pure and R. O. Asplud, J. Coord. Chem. 11 (1981) 73.

10. C. S. Wu, G. R. Rossman, H. B. Gray, G. S. Hammond and H. J. Shugar, Inorg. Chem. (1972) 990.

11. L. S. Kessel and D. N. Hedrickson, Inorg. Chem., 12 (1973) 2630.

12. L. Mishra and M. K. Said, Indian J. Chem., 35A (1996) 304.

13. B. N. Figgis and J. Lewis, Progr. Inorg. Chem., 6 (1964) 97.

14. F. R. Rao, M Sahay and R. C. Aggarwal, Indian J. Chem., 24A (1985) 79.

15. J. Gasso, I. B. Bersuker, J. Garaj, M. Kabesova, J. Kohout, K. Langfelderova, M. Melnik, M. Serator and F. Valach, Coord. Chem. Rev. 19 (1976) 253.

16. K. K. M. Yusuff and C. Krishnakumar, Synth. React. Inorg. Met.-Org. Chem., 23 (1993) 695.

17. R. Sreekala and K. K. M. Yusuff, Synth. React. Inorg. Met.-Org. Chem., 24 (1994) 1773.

18. L. Mishra and M. K. Said, Indian J. Chem. 32A (1993) 417.

19. S. K. Sengupta, S. K. Sahni and R. N. Kapoor, Indian J. Chem., 20A (1981) 692.

20. V. M. Leovak, L. S. Jovanovic, L. J. Bjelica and V. I. Cesljevic, Polyhedron, 8 (1989) 135.

21. K. K. M. Yusuff and A. R. Karthikeyan, Synth. React. Inorg. Met.-Org. Chem., 21 (1991) 903.

22. N. Nawar, M. A. Khattab, M. M. Bekheit and A. H. El. Kaddah, Indian J. Chem., 35A (1996) 308.

23. S. N. Dubey and B. Kaushik, Indian J. Chem. 24A (1985) 950.

24. J. G. Lozano, M. A. M. Lorente, E. Escriva and R. Ballesteros, Synth. React. Inorg. Met.-Org. Chem. 24 (3) (1994) 365.

25. R. H. Holm, A. Chakraworthy and L. J. Theriot, Inorg. Chem., 5 (1966) 625.

CHAPTER VII

CATALYTIC ACTIVITY STUDIES IN THE OXIDATION OF ASCORBIC ACID TO DEHYDROASCORBIC ACID

7.1 INTRODUCTION

Development of catalysis over the past few decades has been characterised by the wide application of metal complexes and organometallic compounds as catalysts. Selective oxidation or oxygenation of organic substances is important in chemical and petrochemical industries due to the wide variety of products synthesised in this route. Much effort has been devoted to develop useful catalytic systems for mild and selective oxidation of organic compounds with the aid of molecular oxygen[1,2].

Ascorbic acid, an important reducing agent in biochemical systems, is easily oxidised by many transition metal centres to dehydroascorbic acid[3-5]. From the chemical point of view, the oxidation of ascorbic acid has been the subject matter of many investigations. A number of papers have been published on the oxidation of ascorbic acid[6-11] catalysed by copper(II) and iron(III) ions. Because of its biochemical significance, most of the studies of the oxidation of ascorbic acid have been carried out in or near the physiological pH range. Certain transition metal complexes of ligands containing quinoxaline ring systems have been found to exhibit catalytic activity towards oxidation of ascorbic acid by molecular oxygen[12]. In this chapter we present our studies on the catalytic activity of Mn(II), Fe(III), Co(II) Ni(II) and Cu(II) complexes of the following Schiff bases towards the oxidation of ascorbic acid.

i. quinoxaline-2-carboxalidene-2-aminophenol,
ii. quinoxaline-2-carboxaldehyde semicarbazone,
iii. quinoxaline-2-carboxalidene-2-furfurylamine and
iv. quinoxaline-2-carboxalidene-*o*-phenylenediamine.

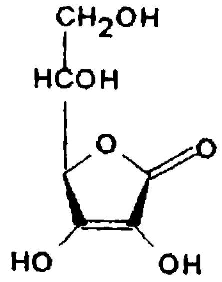


Fig. 7.1 structure of ascorbic acid

7.2 EXPERIMENTAL

7.2.1 *Preparation of Solutions*

a. Ascorbic acid

A 1.0×10^{-3} mol l^{-1} solution of L-ascorbic acid has been prepared in water afresh before each kinetic run.

b Catalyst

Details regarding the synthesis and chracterisation of the metal complexes are given in the previous chapters. All the solutions of the catalysts (1.0 x 10^{-4} mol l^{-1}) were prepared in methanol afresh before each kinetic run.

c Solvent

A 1:1 mixture of methanol and water was used as the solvent for the reaction mixtures.

d Reaction Mixtures

The total volume of the reaction mixture taken was 10 ml. The concentration of the catalyst in all the cases was maintained as 1.0×10^{-6} mol l^{-1} and the catalyst to substrate ratio was kept at 1:100.

7.2.2 *Apparatus*

A Shimadzu UV-Vis 160A spectrophotometer with 1 cm quartz cells is used for absorbance measurements.

7.2.3 *Kinetic Procedure*

All kinetic runs were carried out at a temperature of 28.0 ± 0.1 ^{o}C. Requisite amounts of all the reagents except ascorbic acid were taken in a reaction bottle. The reaction was initiated by transferring the calculated amount of ascorbic acid into the reaction bottle. The reaction is monitored by following the absorbance of ascorbic acid at 265 nm, where it has maximum absorbance and all other substances present in the reaction mixture have negligible absorbance. The concentration of ascorbic acid was obtained from the absorbance data using a molar absorption coefficient of 7500 at 265 nm.

The initial rates of the reaction were obtained by fitting the concentration versus time data into a polynomial of the form

$$c = a_1 + a_2t + a_3t^2 + \ldots$$

and obtaining the slope of the curve[13] at t=0. A software called "axum" (Trimetrix, 1989) was used for this purpose. All the kinetic results were found to be reproducible within an error of ± 5 %.

7.3 RESULTS AND DISCUSSION

The results of the study of catalytic activity of the synthesised complexes are given in Table VII.1.

The data indicate that among the various metal complexes synthesised all the complexes of copper(II) were found to show significant catalytic activity in the oxidation of ascorbic acid to dehydroascorbic acid and none of the manganese(II) complexes were catalytically active. Next to the copper complexes, iron(III) complex of the ligand QOD has the maximum activity. Apart from these complexes QAP complexes of cobalt(II) and nickel(II), QFA complex of iron(III), QSC complexes of nickel(II) and iron(III) and QOD complex of cobalt(II) also have a slight catalytic activity. Among all the copper(II) complexes, the complex of the ligand QSC was found to be the most active

Table VII.1

Rate of Catalytic Oxidation of Ascorbic Acid

[Ascorbic acid] = 1.0×10^{-4} *mol* l^{-1}
[Catalyst] = 1.0×10^{-6} *mol* l^{-1}

Catalyst	Rate of conversion (mol $l^{-1}s^{-1}$) x 10^{9}
——	2.29
[Mn(QAP)$_2$]	3.69
[Fe(QAP)$_2$Cl]	3.80
[Co(QAP)$_2$]	13.3
[Ni(QAP)$_2$]	7.27
[Cu(QAP)$_2$]	103.15
[Mn(QSC)Cl$_2$]	1.45
[Fe(QSC)Cl$_3$]	8.03
[Co(QSC)$_2$]	2.14
[Ni(QSC)Cl]	23
[Cu(QSC)Cl]	1050
[Mn(QFA)$_2$Cl$_2$]	3.56
[Fe(QFA)(OH)$_2$Cl]	5.08
[Co(QFA)$_2$Cl$_2$]	0.59
[Ni(QFA)$_2$Cl$_2$]	1.4
[Cu(QFA)Cl$_2$]	549.73
[Mn(QOD)Cl$_2$]	2.22
[Fe(QOD)Cl$_3$]	315.98
[Co(QOD)Cl$_2$]	6.68
[Ni(QOD)Cl$_2$]	3.19
[Cu(QOD)Cl$_2$]	444.01

catalyst. The results are presented as block diagrams in Figures 7.2-7.5.

Ascorbic acid is found to be oxidised by several iron(III) and copper(II) chelates[6]. In most of these studies the rate was found to be independent of the partial pressure of oxygen. A dissociative mechanism has been assumed for the reaction. Hence it is proposed that the stability of the metal chelates and the steric factors related to the orientation and dimensions of the ligand donor groups can affect the rate[6].

The present investigation indicated that in spite of the considerable variation in the structure and stability, all the copper complexes were found to be active, while in the case of the other complexes, the slight activity observed has no regular dependence on either the nature of the ligand or the structure of the complexes as a whole. Thus it can be inferred that the catalytic activity of the synthesised complexes of the Schiff bases derived from quinoxaline-2-carboxaldehyde is highly influenced by the nature of the metal ion involved. But it is not clear whether dissociative type of mechanism is operative in these studies also.

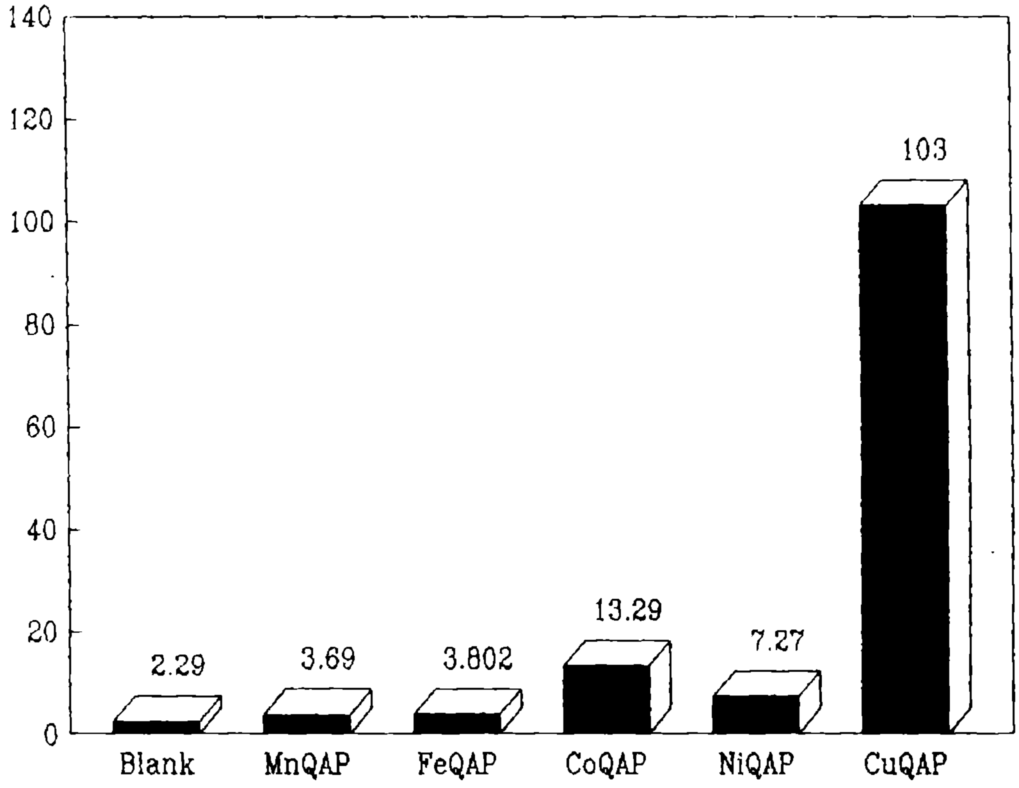


Fig. 7.2 Catalytic activity of Complexes of QAP.

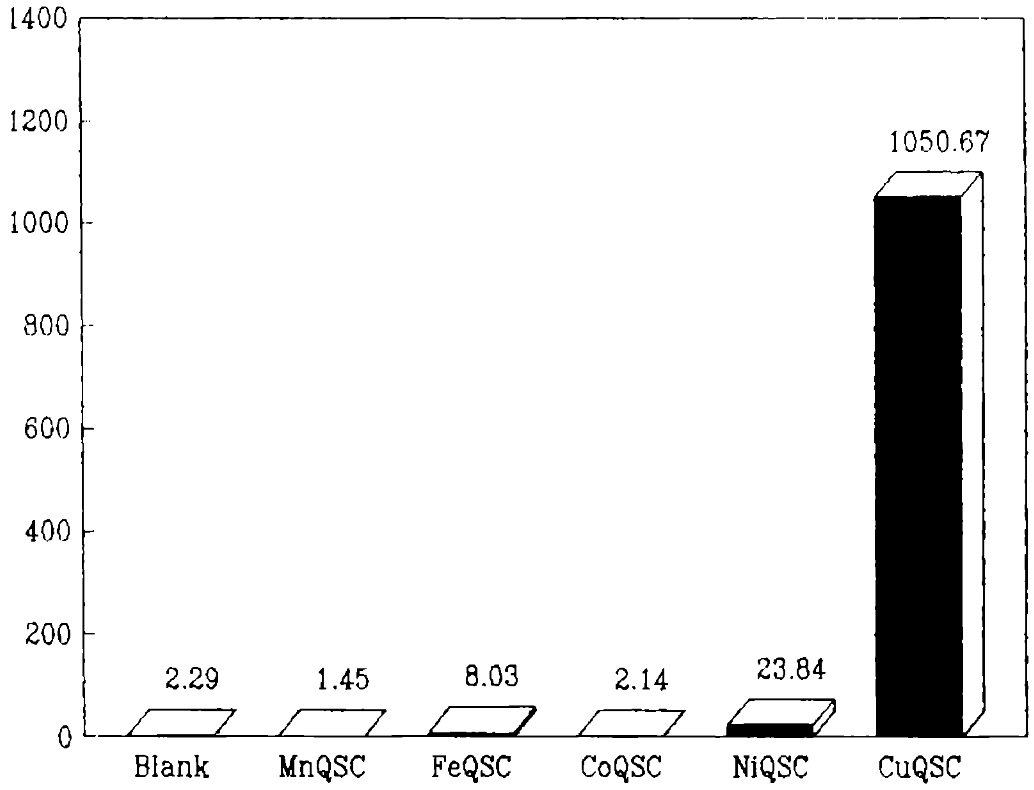


Fig. 7.3 Catalytic activity of Complexes of QSC

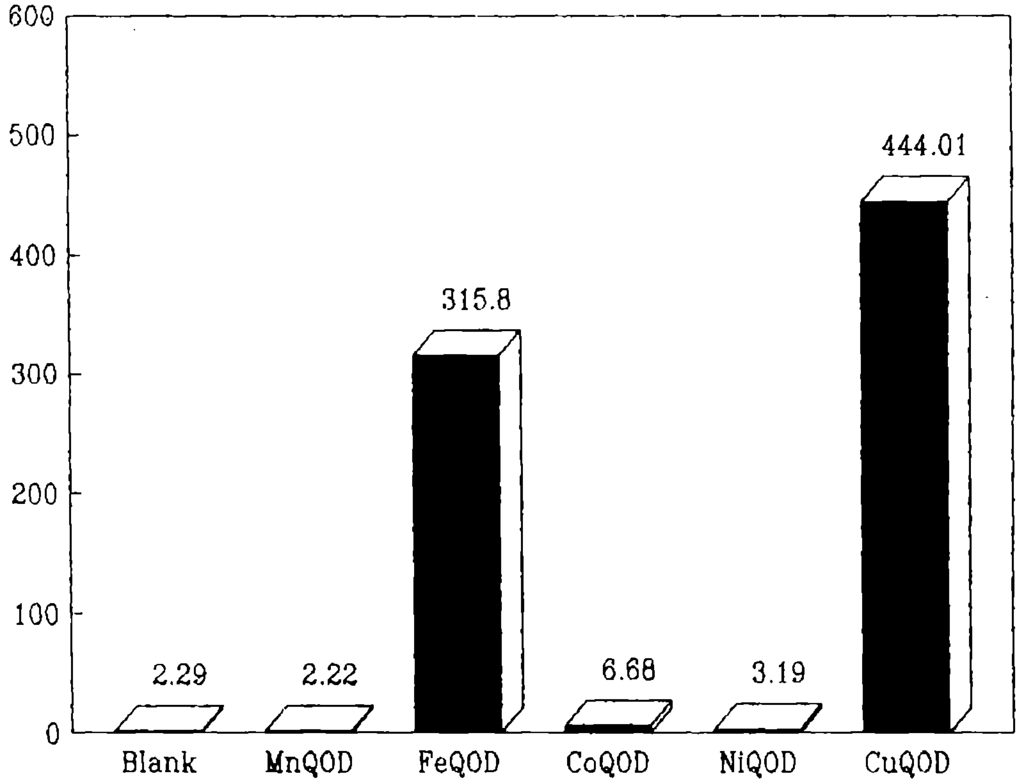


Fig. 7.4 Catalytic activity of Complexes of QOD

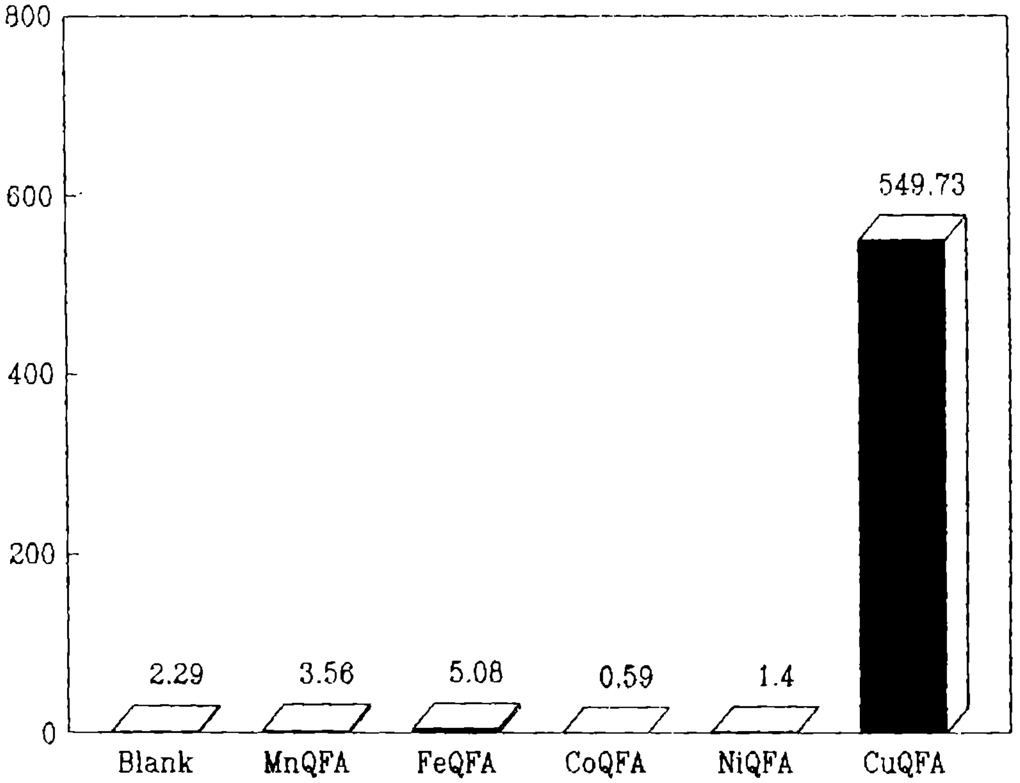


Fig. 7.5 Catalytic activity of Complexes of QFA

REFERENCES

1. R.A.Sheldon, J. K. Kochi "Metal catalysed oxidation of organic compounds", Academic Press, New York (1981).

2. A.E.Martell, D. T. Sawyer "Oxygen complexes and oxygen activation by transition metals", Eds., Plenum, New York (1988).

3. S. P. Mushran, M. C. Agarwal, J. Sci. Ind. Res., 36 (1977) 274.

4. E. Y. Shtamma, A. P. Puermal, Y. J. Scurlatov, Int. J. Chem. Kinet., 11 (1979) 1979.

5. B. Banas, Inorg. Chim. Acta Lett., LI3 53 (1981).

6 M. M. T. Khan and A. E. Martell, J. Am. Chem. Soc., 89 (1967) 4176 .

7. P. Martinez and D. Uribe, Ann. Quim., 76 (1987) 201.

8. U. S. Mehrotre, M. C. Agarwal and S. P. Mushran, J. Phys. Chem., 73 (1969) 96.

9. L. Ferrai and A. Alonso, Ann. Quim., 79 (1983).

10. B. Bansch, P. Martinez, J. Zuluaga, D. Uribe and R. Van Eldik, Z. Phys. Chem., 170 (1991) 59.

11. P. Martinez, J. Zuluaga, D. Uribe and R. Van Eldik, Inorg.Chim. Acta, 136 (1987) 11.

12. Jose Mathew, Ph.D.Thesis, Cochin University, Kochi, Kerala, India (1995).

13. N. Sridevi, Ph.D. Thesis, Andhra University, Visakhapatnam, Andhra Pradesh, India (1991).

CHAPTER VIII

KINETIC STUDY OF THE OXIDATION OF ASCORBIC ACID CATALYSED BY THE COPPER(II) COMPLEX OF QUINOXALINE-2-CARBOXALIDENE-2-AMINOPHENOL

8.1 INTRODUCTION

The kinetics and mechanism of metal ion catalysis in the oxidation of ascorbic acid have been the subject matter of several studies. The catalytic oxidation of ascorbic acid in the presence of Cu(II) and Fe(III) ions and their complexes in aqueous medium have been reported[1-6]. As has been mentioned in the previous chapter, among the various metal complexes synthesised, only the Cu(II) complexes were found to be good catalysts towards oxidation of ascorbic acid. It was therefore found interesting to understand the mechanism of oxidation of ascorbic acid in the presence of these copper complexes. For this purpose, the $[Cu(QAP)_2]$ complex has been chosen as the catalyst and a detailed kinetic study of the oxidation of ascorbic acid in methanol-water mixtures was carried out. The results of these studies are presented in this chapter.

8.2 EXPERIMENTAL

8.2.1 *Materials and Methods*

The procedures employed for the preparation of the solutions and the kinetic procedure employed were the same as that in the screening studies and are presented in Chapter VII.

8.3 RESULTS AND DISCUSSION

RESULTS

8.3.1. *Order with respect to the catalyst*

In order to determine the order with respect to the catalyst, kinetic runs were carried out at constant concentration of ascorbic acid and at constant composition of the solvent, varying the concentration of the solvent from 1.0 x 10^{-5} mol l^{-1} to 1.0 x 10^{-6} mol l^{-1} and the corresponding initial rates were obtained. These results are tabulated in table VIII.1. The initial rate of the reaction is found to be increasing with increasing concentration of the catalyst. A plot of initial rate versus [complex] (Fig.8.1) is found to be a straight line,

Table VIII.1

Effect of varying catalyst concentration on the initial rate

[ascorbic acid] = 1.0x10^{-4} mol l^{-1}

dielectric constant of solvent (D) = 55.58

[catalyst] x 10^6 M	initial rate x 10^8 (mol l^{-1} s^{-1})
1.0	2.2
2.0	5.0
6.0	15.0
10.0	25.3

passing through the origin, indicating order with respect to the catalyst to be one.

8.3.2. *Order with respect to ascorbic acid*

To determine the order with respect to ascorbic acid, kinetic runs were performed at constant concentration of the catalyst and at constant composition of the solvent, varying the concentration of ascorbic acid from 2.0 x 10^{-4} mol l^{-1} to 2.0 x 10^{-5} mol l^{-1}. The concentration of the catalyst employed was 1.0 x 10^{-6} mol l^{-1}, and a 1:1 mixture of methanol and water was used as the solvent. Under such conditions, the initial rate of the reaction is found to remain constant within the limits of experimental error. It can therefore be inferred that the reaction is zero order with respect to ascorbic acid.

8.3.3. *Effect of ligand*

For studying the effect of ligand, the oxidation of ascorbic acid was performed in the presence of added ligand in addition to all the other reagents. Kinetic runs were carried out at constant concentrations of ascorbic acid and catalyst and at constant composition of the solvent, varying the concentration of the added ligand from 1.0 x 10^{-6} mol l^{-1} to 1.0 x 10^{-5} mol l^{-1}. The initial rate of the reaction is found to be decreasing with increase in added ligand concentration. The results of this study are presented in table VIII.2. A plot of reciprocal of the initial rate versus [ligand] is found to be a straight line with an intercept on the rate-axis as shown in figure, 8.2.

Table-VIII.2

Effect of added ligand on the initial rate

[ascorbic acid] = 1.0×10^{-4}.M
[catalyst] = 1.0×10^{-6} M
dielectric constant (D) = 55.58

[ligand] x 10^6 (M)	initial rate x 10^8 (mol l^{-1} s^{-1})
0.0	2.7
1.0	2.2
6.0	1.9
8.0	1.7
10.0	1.5

8.3.4 *Effect of composition of the solvent*

To study the effect of polarity of the solvent on the rate, kinetic runs were carried out at constant concentrations of catalyst and ascorbic acid, varying the composition of the solvent. The dielectric constant (D) of the solvent is calculated assuming linear relationship of dielectric constant with composition. The results obtained are presented in table VIII.3. A plot of 1/D versus log(initial rate) is found to be a straight line with negative slope, as shown in Figure 8.3. From this plot it can be inferred that, the undissociated acid is the reactive species in this reaction.

Table–VIII.3

Effect of varying solvent dielectric constant

[ascorbic acid] = 1.0x10^{-4} mol l^{-1}
[catalyst] = 2.0x10^{-6} mol l^{-1}

solvent dielectric constant (D)	initial rate x 10^{8} (mol l^{-1} s^{-1})
60.17	2.2
57.89	3.3
55.58	4.3
53.29	6.5
50.99	13.6

8.3.5 *Self decomposition of the complex*

In order to study the self decomposition of the complex, reaction was carried out in the absence of ascorbic acid, in 1:1 methanol-water mixtures employing the concentration of the complex as 1.0 x 10^{-5} mol l^{-1}. The reaction was initiated by transferring the catalyst solution into the solvent and was monitored by following the absorbance of the complex at 235 nm. From this study, the initial rate of self decomposition of the complex was determined to be 3.5 x 10^{-10} mol l^{-1} s^{-1}.

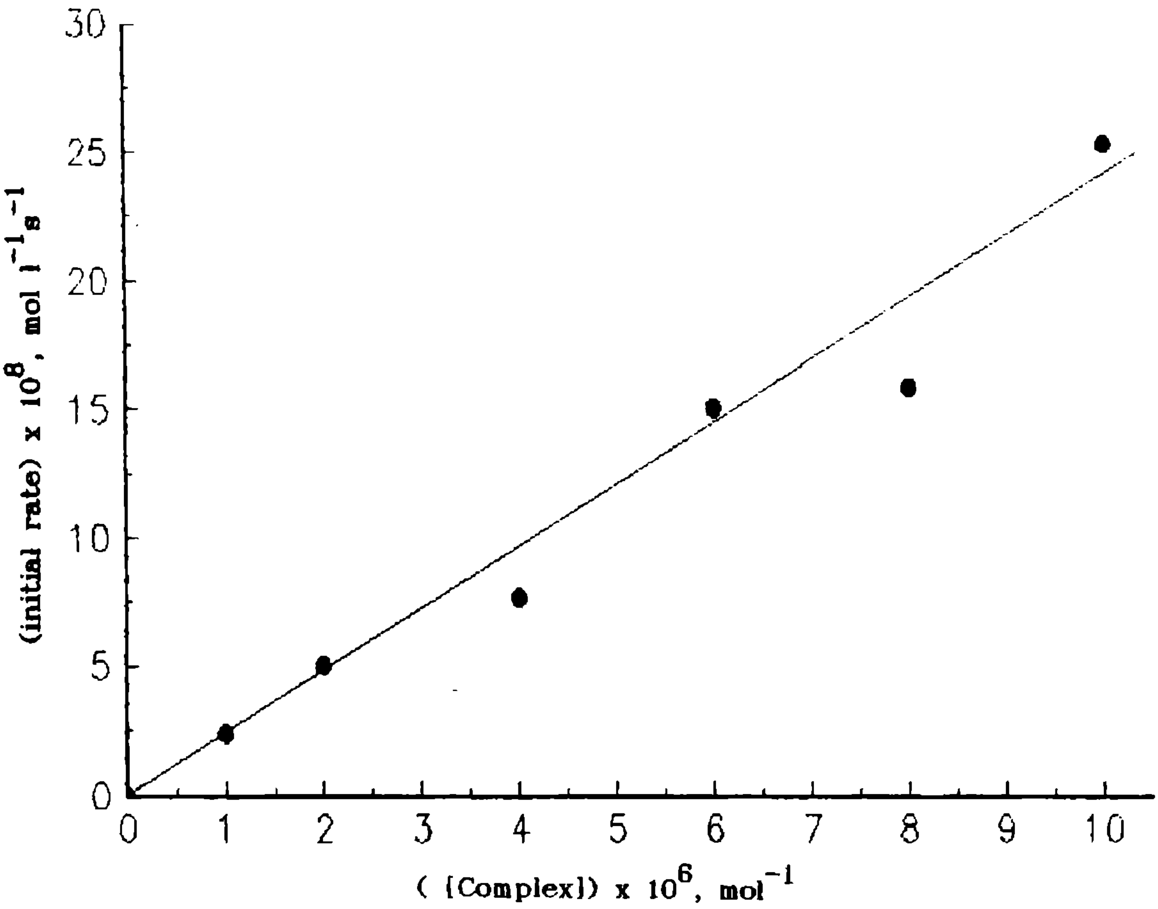


Fig. 8.1 Plot of initial rate versus $[Cu(QAP)_2]$

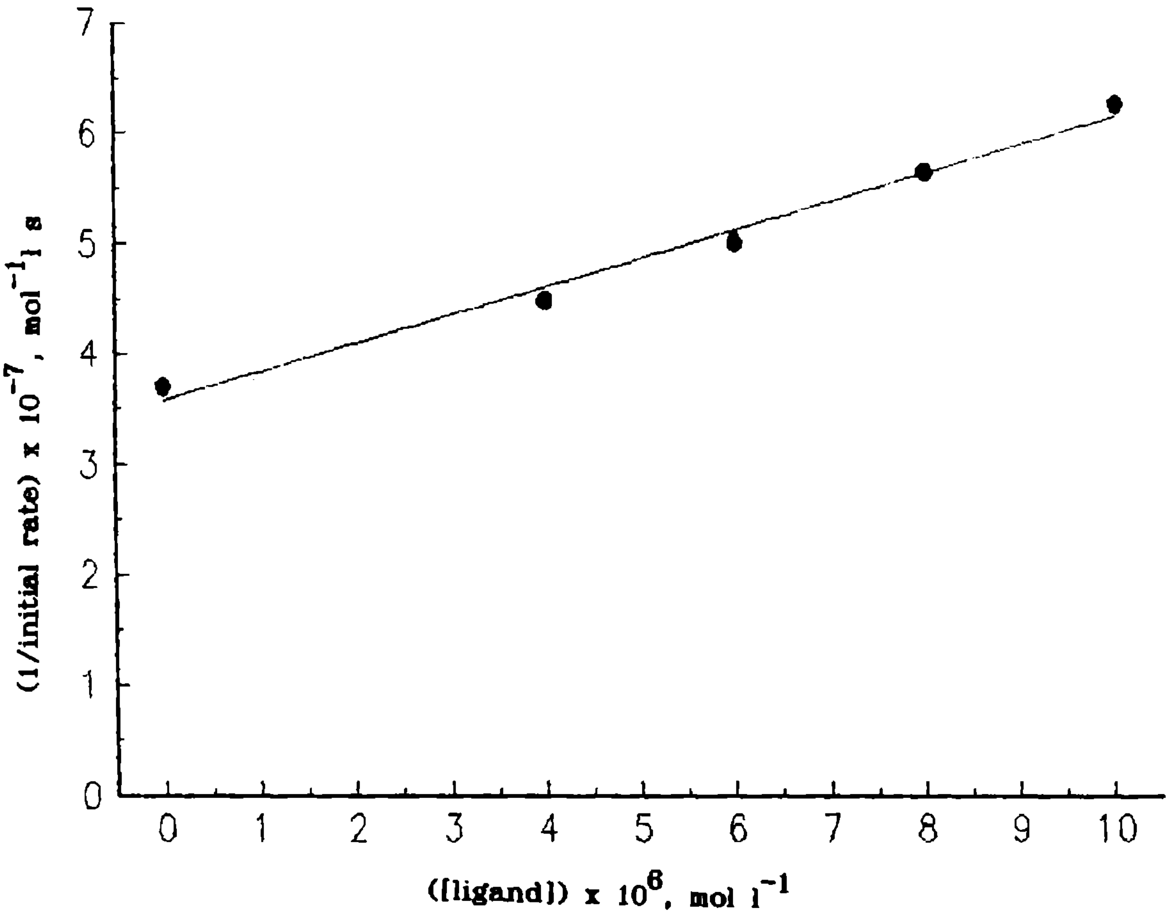


Fig. 8.2 Plot of (1/ initial rate) versus [ligand]

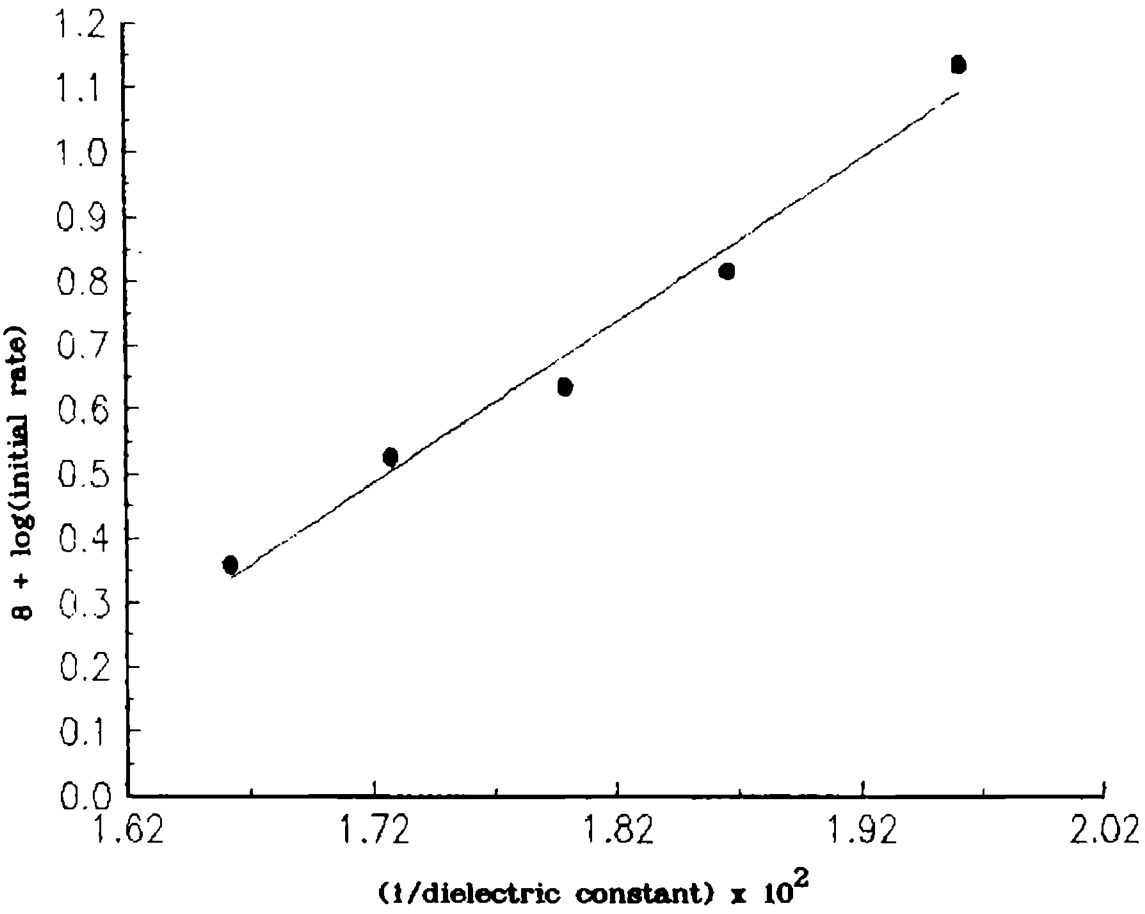


Fig. 8.3 Plot of (1/D) versus log(initial rate)

DISCUSSION

To summarise the observed results, the rate of the reaction is found to be first order with respect to the catalyst and zero order with respect to ascorbic acid. In the presence of added ligand the initial rate of the reaction is found to be decreasing with increase in ligand concentration. When the composition of the solvent was varied, it is found that a plot of 1/D versus log(initial rate) is a straight line with a negative slope. The observed solvent effect indicates that undissociated acid is the reactive species.

The zero order dependence of the initial rate of the reaction on [ascorbic acid] gives a first impression that the mechanism of the reaction involves the oxidation of the catalyst by molecular oxygen in a slow step, followed by a fast step in which ascorbic acid is oxidised. If this is the mechanism of the reaction the rate determining step should be independent of [ascorbic acid]. In that case the rate of the reaction should be equal to the rate of oxidation of the complex in the absence of ascorbic acid. However, when the rate of decomposition of the complex was monitored in the absence of ascorbic acid, even at the highest concentration of the complex that has been employed in the catalysed reaction, the rate of decomposition of the complex was much less than that of the oxidation of ascorbic acid. Therefore, in order to explain the observed zero order dependence of initial rate with respect to ascorbic acid, the formation of an intermediate between the complex and asocrbic acid which further reacts with molecular oxygen has been presumed. Further, the observed ligand effect indicates that either the catalyst exists as an equilibrium mixture of two species, as may be expressed by the following equation

$$ML_2 \rightleftharpoons ML + L$$

where ML_2 is the undissociated complex and ML is the monodissociated species, or due to the ligand being liberated during the formation of the intermediate between the complex and ascorbic acid.

On the basis of the obseved results, the mechanism of the reaction in the first case may be assumed to be the one given below:

$$Cu^{II}L_2 \overset{K}{\rightleftharpoons} Cu^{II}L + L \qquad —1$$

$$Cu^{II}L + AA \overset{K_1}{\rightleftharpoons} Cu^{II}L(AA) \qquad —2$$

$$Cu^{II}L(AA) \xrightarrow[slow]{k} DHA + Cu^{I}L \qquad —3$$

$$Cu^{I}L + O_2 \xrightarrow{fast} Cu^{II}L \qquad —4$$

where $Cu^{II}L_2$ represents the undissociated complex, and $Cu^{II}L$ is the mono dissociated species, AA and DHA represent ascorbic acid and dehydroascorbic acid respectively, and the species formed by the interaction of AA with $Cu^{II}L$ is represented by $Cu^{II}L(AA)$. $Cu^{I}L$ is the reduced form of the species $Cu^{II}L$ and it is oxidised back to $Cu^{II}L$ by molecular oxygen.

This mechanism leads to the rate equation,

$$\text{Rate} = k[\mathrm{Cu^{II}L(AA)}]_e \qquad \text{—5}$$

From equation 2 we obtain,

$$[\mathrm{Cu^{II}L(AA)}]_e = K_1[\mathrm{Cu^{II}L}]_e[\mathrm{AA}]_e \qquad \text{—6}$$

Substituting for $[\mathrm{Cu^{II}L(AA)}]_e$ from equation 6, in equation 5 we can get,

$$\text{Rate} = kK_1[\mathrm{Cu^{II}L}]_e[\mathrm{AA}]_e \qquad \text{—7}$$

Taking,

$$[\mathrm{Cu^{II}L}] = [\mathrm{Cu^{II}L}]_e + [\mathrm{Cu^{II}L(AA)}]_e \qquad \text{—8}$$

and by substituting for $[\mathrm{Cu^{II}L(AA)}]$ from equation 6 in equation 8,

$$[\mathrm{Cu^{II}L}] = [\mathrm{Cu^{II}L}]_e + K_1[\mathrm{CuL}]_e[\mathrm{AA}]_e \qquad \text{—9}$$

$$[\mathrm{Cu^{II}L}]_e = \frac{[\mathrm{Cu^{II}L}]}{\{1 + K_1[\mathrm{AA}]_e\}} \qquad \text{—10}$$

Hence the rate equation 7 becomes,

$$\text{Rate} = \frac{kK_1[\mathrm{Cu^{II}L}][\mathrm{AA}]_e}{\{1 + K_1[\mathrm{AA}]_e\}} \qquad \text{—11}$$

If $1 \ll K_1[\mathrm{AA}]_e$ the rate equation reduces to,

$$\text{Rate} = k[\mathrm{Cu^{II}L}] \qquad \text{—12}$$

But

$$[\mathrm{cat}]_t = [\mathrm{Cu^{II}L_2}] + [\mathrm{Cu^{II}L}] \qquad \text{—13}$$

where $[cat]_t$ represents the total concentration of all the species of the catalyst. From equation 1,

$$K = \frac{[Cu^{II}L][L]}{[Cu^{II}L_2]} \qquad \text{—14}$$

Therefore equation 13 becomes,

$$[cat]_t = \frac{[Cu^{II}L][L]}{K} + [Cu^{II}L] \qquad \text{—15}$$

Or

$$[Cu^{II}L] = \frac{K[cat]_t}{\{K + [L]\}} \qquad \text{—16}$$

Then equation 12 may be written as,

$$Rate = \frac{kK[cat]_t}{\{K + [L]\}} \qquad \text{—17}$$

Now if K << [L] the rate equation reduces to,

$$Rate = \frac{kK[cat]_t}{[L]} \qquad \text{—18}$$

Since [L] represents the total concentration of the ligand present in the solution, it includes the concentration of the ligand formed from equilibrium 1 as well as the concentration of the ligand added. If we represent the former as $[L]_i$ and the latter as $[L]_a$, we obtain the rate equation as

$$Rate = \frac{kK[cat]_t}{\{[L]_i + [L]_a\}} \qquad \text{—19}$$

Rearranging equation 19,

$$\frac{1}{\text{Rate}} = \frac{[L]_i}{kK[\text{cat}]_t} + \frac{[L]_a}{kK[\text{cat}]_t} \qquad \text{—20}$$

Equation 20 indicates that a plot of 1/(initial rate) versus $[L]_a$ should be a straight-line with an intercept on the rate-axis, provided $[L]_i$ is a constant.

Considering the other case, if the observed ligand effect is due to the liberation of the ligand during the formation of the intermediate between the catalyst and ascorbic acid, then the mechanism of the reaction may be represented as given below:

$$\text{Cu}^{\text{II}}\text{L}_2 + \text{AA} \xrightarrow{K'} \text{Cu}^{\text{II}}\text{L(AA)} + \text{L} \qquad \text{—(21)}$$

$$\text{Cu}^{\text{II}}\text{L(AA)} \xrightarrow[\text{(slow)}]{k'} \text{Cu}^{\text{I}}\text{L} + \text{DHA} \qquad \text{--(22)}$$

$\text{Cu}^{\text{I}}\text{L}$ is then oxidised by molecular oxygen to give $\text{Cu}^{\text{II}}\text{L}$ in a fast step.

This mechanism leads to the rate equation

$$\text{Rate} = k'[\text{Cu}^{\text{II}}\text{L(AA)}]_e \qquad \text{—(23)}$$

But from equation (21), we get,

$$[\mathrm{Cu^{II}L(AA)}]_e = \frac{K'[\mathrm{Cu^{II}L_2}]_e[\mathrm{AA}]_e}{[\mathrm{L}]_e} \quad \text{—(24)}$$

Substituting for $[\mathrm{Cu^{II}L(AA)}]_e$ in equation (23),

$$\mathrm{Rate} = \frac{k'K'[\mathrm{Cu^{II}L_2}]_e[\mathrm{AA}]_e}{[\mathrm{L}]_e} \quad \text{—(25)}$$

The total concentration, $[\mathrm{Cu^{II}}]_t$, of all the species of $\mathrm{Cu^{II}}$ in solution may be given as

$$[\mathrm{Cu^{II}}]_t = [\mathrm{Cu^{II}L_2}]_e + [\mathrm{Cu^{II}L(AA)}]_e \quad \text{—(26)}$$

After substituting for $[\mathrm{Cu^{II}L(AA)}]_e$ from equation (24), equation (26) can be written as,

$$[\mathrm{Cu^{II}}]_t = [\mathrm{Cu^{II}L_2}]_e + \frac{K'[\mathrm{Cu^{II}L_2}]_e[\mathrm{AA}]_e}{[\mathrm{L}]_e} \quad \text{—(27)}$$

Equation (27) can be rearranged as below:

$$[\mathrm{Cu^{II}}]_t = \frac{[\mathrm{Cu^{II}L_2}]_e \,\{\, [\mathrm{L}]_e + K'\,[\mathrm{AA}]_e\}}{[\mathrm{L}]_e} \quad \text{--(28)}$$

Hence $[Cu^{II}L_2]_e$ can be expressed by the following equation:

$$[Cu^{II}L_2] = \frac{[Cu^{II}]_t \ [L]_e}{\{ [L]_e + K' \ [AA]_e\}} \qquad \text{—(29)}$$

Assuming $[AA]_e$ is equal to the total concentration of ascorbic acid, $[AA]$, from equations (25) and (29), we get,

$$\text{Rate} = k'K' \ \frac{[Cu^{II}]_t[L]_e[AA]}{\{[L]_e + K'[AA]\}} \qquad \text{—(30)}$$

If $K'[AA] \gg [L]_e$ then equation (30) reduces to

$$\text{Rate} = k' \ [Cu^{II}]_t \qquad \text{—(31)}$$

This may be the case in the absence of added ligand. But probably when the ligand is added $[L]_e$ is no longer negligible compared to $K'[AA]$. Under such conditions if it is assumed that the concentration of the ligand at equilibrium is equal to the concentration of the ligand added, equation (30) becomes,

$$\text{Rate} = \frac{k'K'[Cu^{II}]_t[AA]}{\{[L] + K'[AA]\}} \qquad \text{—(32)}$$

Equation (32) may be rearranged as,

$$\frac{1}{\text{Rate}} = \frac{[L]}{k'K'[Cu^{II}]_t[AA]} + \frac{1}{k'[Cu^{II}]_t} \qquad \text{--(33)}$$

This equation indicates that at constant concentrations of AA and the catalyst, 1/rate versus [L] should be a straight line with an intercept on the rate axis, as has been observed.

Thus both the proposed mechanisms can explain all the kinetic results obtained.

In both the proposed mechanisms, the rate determining step involves dissociation of the intermediate species formed between the catalyst and ascorbic acid. Formation of such an intermediate should obviously be easier for complexes involving less bulky ligands. Among the various ligands employed, QSC may be considered to be the smallest ligand as the amine part does not contain bulky aromatic ring systems as in the other cases. This is probably the cause for the much higher activity of the $[Cu(QSC)Cl_2]$ complex compared to the other three copper complexes.

REFERENCES

1. E. S. G. Barron, R. De Meio, and F. W. Klemperor, J. Biol. Chem., 112 (1936) 625.
2. A. Weissberger, J. E. Luvalle, and D. S. Thomas, Jr., J. Am. Chem. Soc., 65 (1943) 1934.
3. A. Weissberger, J. E. Luvalle, J. Am. Chem. Soc., 66 (1944) 700.
4. H. Nord, Acta Chim. Scand., 9 (1955) 442.
5. R. Grinstead, J. Am. Chem. Soc., 82 (1956) 3464.
6. A. O. Dekker and R. G. Dikkinson J. Am. Chem. Soc., 62 (1940) 2165.

SUMMARY

The thesis deals with the synthesis, characterization and catalytic activity studies of some new transition metal complexes of Schiff bases derived from quinoxaline–2–carboxaldehyde.

The thesis is divided into eight chapters. Chapter I of the thesis presents an introduction to metal complexes of Schiff bases derived from various aldehydes, like salicylaldehyde, pyridine–2–carboxaldehyde and quinoxaline–2–carboxaldehyde. The scope of the present investigation is also outlined in this chapter. Chapter II gives the procedures for the synthesis of Schiff base ligands and the experimental procedures involved in the study.

Chapters III, IV, V and VI deal with the studies on the synthesis and characterisation of complexes of the Schiff base ligands obtained by the interaction of quinoxaline–2–carboxaldehyde with 2–aminophenol, semicarbazide, *o*–phenylene diamine or furfurylamine. The results of our studies on the manganese(II), iron(III), cobalt(II), nickel(II) and copper(II) complexes of the Schiff base, quinoxaline–2–carboxalidene–2–aminophenol (QAP) are presented in ChapterIII. All the complexes are non–electrolytes in nitrobenzene. The complexes have the general formula $[M(QAP)_2]$, where M =

manganese(II), cobalt(II), nickel(II) or copper(II). The formula of the iron(III) complex is $[Fe(QAP)_2Cl_2]$. The IR spectral studies of the complexes indicate that the Schiff base binds to the metal through the nitrogen atom of the azomethine group and through the hydroxyl oxygen atom, the latter is coordinated to the metal atom in the ionised form. Magnetic and electronic spectral data suggest a tetrahedral structure for the manganese(II), cobalt(II) and nickel(II) complexes, a distorted tetrahedral structure for the copper(II) complex and an octahedral dimeric structure with bridging chlorine atom for the iron(III) complex respectively.

Chapter IV deals with the synthesis and characterisation of manganese(II), iron(III), cobalt(II), nickel(II) and copper(II) complexes of the Schiff base, quinoxaline-2-caboxaldehyde semicarbazone (QSC). The complexes are non-electrolytes in nitrobenzene. With the exception of the iron(III) complexes, all the complexs have the general formula $[M(QSC)Cl_2]$. The formula of the iron(III) complex is $[Fe(QSC)Cl_3]$. IR spectral studies of these complexes show that in the case of the iron(III) complex QSC acts as a tridentate ligand, coordinating through the azomethine nitrogen atom, the ring nitrogen atom and the carbonyl oxygen atom where as in all the other complexes binding through the carbonyl oxygen atom is absent and it acts as a bidentate ligand. Magnetic and electronic spectral data of the complexes reveal a tetrahedral structure for the manganese(II), cobalt(II) and nickel(II) complexes, an octahedral structure for the iron(III) complex and a square planar structure for the copper(II) complex. EPR spectrum of the copper(II) complex is similar to that of other reported cases of square planar copper(II) complexes.

Chapter V gives details about our studies on the manganese(II), iron(III), cobalt(II), nickel(II) and copper(II) complexes of the Schiff base, quinoxaline-2-carboxalidene-o-phenylenediamine (QOD). Conductivity measurements in acetonitrile indicate the non-electrolytic nature of the complexes. The general formula of the manganese(II), cobalt(II), nickel(II) and copper(II) complexes is $[M(QOD)Cl_2]$. The iron(III) complex has the formula $[Fe(QOD)Cl_3]$. IR spectra indicate that the ligand binds the metal ion using its azomethine nitrogen and primary amino group in the case of manganese(II), cobalt(II), nickel(II) and copper(II) complexes. In the case of the iron(III) complex, the ring nitrogen also takes part in complexation. From the magnetic moment values and electronic spectral data, a tetrahedral structure has been assigned for the manganese(II), cobalt(II) and nickel(II) complexes. An octahedral and distorted tetrahedral geometries have been proposed for the iron(III) and copper(II) complexes respectively.

Chapter VI presents the studies on the manganese(II), iron(III), cobalt(II), nickel(II) and copper(II) complexes of the Schiff base, quinoxaline-2-carboxalidene-2-furfurylamine (QFA). All these complexes are found to be non-electrolytes in nitrobenzene. The general formula of manganese(II), cobalt(II) and nickel(II) complexes is $[M(QFA)_2Cl_2]$, while the formulae of iron(III) and copper(II) complexes are $[Fe(QFA)(OH)_2Cl]$ and $[Cu(QFA)Cl_2]$ respectively. IR spectra of the complexes indicate that in all the complexes, the ligand QFA acts as a bidentate ligand coordinating through the azomethine nitrogen and ring nitrogen. Magnetic and electronic spectral data suggest that the manganese(II), cobalt(II) and nickel(II) complexes have an octahedral structure, whereas the iron(III) complex has an octahedral dimeric structure, involving hydroxo bridges. A distorted tetrahedral structure has been assigned for the copper(II) complex.

Chapter VII deals with the catalytic activity studies of the synthesised complexes towards the oxidation of ascorbic acid to dehydroascorbic acid by molecular oxygen. The catalytic activity of the complexes has been determined by measuring the rate of decomposition of ascorbic acid in the presence of the complexes and by comparing these rates with the rate of self-decomposition of the acid under similar experimental conditions. This study indicated that among the various complexes used, all the copper(II) complexes were found to be catalytically active and none of the manganese(II) complexes were active. Among the various copper(II) complexes, the complex of the ligand, QSC was found to be the most active. A few of the iron(III), nickel(II) and cobalt(II) complexes were also found to be slightly active. However, no correlation between the type of the ligand present in the complex and the catalytic activity of the latter could be drawn.

Chapter VIII deals with our attempt to explain the observed catalytic activity of the copper complexes in terms of the mechanism of the catalysed reaction. In order to determine the mechanism of the catalysed reaction, copper(II) complex of the ligand QAP was chosen and a detailed kinetic study of the decomposition of ascorbic acid in the presence of this complex was made in methanol-water mixtures. The concentration versus time data obtained by performing kinetic runs at different initial concentrations of ascorbic acid, catalyst or ligand or at different solvent compositions, were interpreted by employing initial rate method, which indicated the reaction to be of first order with respect to the catalyst and zero order with respect to ascorbic acid. Variation in the composition of the solvent employed causes variation in the rate of the reaction, and a plot of logarithm of the initial rate against the reciprocal of the dielectric constant of the medium employed was found to be linear with negative slope. In the presence of added ligand, the rate of the reaction was found to decrease and a plot of

reciprocal of the initial rate versus added ligand concentration was found to be linear. Two possible mechanistic schemes were proposed to explain the observed results. In either case the reaction is believed to proceed through the formation of an intermediate species between the catalyst and ascorbic acid which decomposes in the rate determining step. The difference in the two schemes arises due to the possible explanation of the observed ligand effect, which can be assigned either to the existence of a dissociation equilibrium for the complex through which a monoligand species is formed or can be attributed to the liberation of a ligand molecule during the formation of an intermediate between the catalyst and ascorbic acid. Rate expressions are derived for each of the mechanistic schemes.